METALLURGY

E. L. RHEAD

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METALLURGY

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METALLURGY

AN ELEMENTARY TEXT-BOOK

BY

E. L. RHEAD

M.Sc. TECH., F.I.C., A.I.M.E., ETC.

FORMERLY LECTURER ON METALLURGY AT THE MUNICIPAL COLLEGE OF TECHNOLOGY
AND IN THE UNIVERSITY OF MANCHESTER
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PREFACE TO THE NEW EDITION

In preparing this new edition of Metallurgy the sequence of former editions has been maintained in order to develop the subject in a progressive manner, and secure the primary object of the book—to inculcate and emphasize the importance of first principles.

Some deletion and condensation of matter has been done, and a considerable amount has been rewritten and rearranged. Large additions have been made in many sections, in order to retain the comprehensive character of the original and to ensure that it will continue to appeal as an introduction of the subject to the practical man in industries dependent on metallic material.

New sections have been added on pyrometry, metallography, and foundry work containing sufficient fundamental matter to serve as a basis for further study while illustrating the matters dealt with. Notable additions have been made in the sections dealing with physical tests, fuel, especially modern coking plant, electric furnaces for steel manufacture and other melting and smelting processes, also, much matter dealing with developments in wet and dry processes for both base and precious metals has been added.

The author wishes to express his thanks to Mr. A. H. Goodger, M.Sc. Tech., and Mr. R. Macfee for their continued assistance, and to Messrs. Avery, Ltd., The Electric Furnace Co., Ltd., The Coppée Co., Ltd., Koppers Coke Oven Co., Ltd., Integra Co. (Birmingham), The Cambridge Scientific Instrument Co., Messrs. E. G. Herbert, and to "Metallurgia," and The Scientific Publishing Co. for permission to use illustrations or the loan of blocks.

While maintaining the form of the text-book some additions and rearrangements have been made. Certain processes have assumed an importance in recent years that an extended notice was necessary. Those which it was inconvenient to incorporate in the text, have been dealt with in the appendices.

In addition to previous acknowledgments, the author wishes to thank Messrs. Huntington Heberlein & Co., Ltd., and the Deister Concentrator Company for permission to use drawings and illustrations.

E. L. RHEAD.

MANCHESTER.
June, 1939.

PREFACE TO THE FIRST EDITION

IN issuing this little work the author has endeavoured to provide the student with a book of moderate size, giving a clear and concise account of metallurgical processes, and the principles upon which they are based. Details are given only when necessary for the sake of clearness.

The chemical changes involved in the various processes described are specially dealt with, but it must be remembered that the equations given for reactions occurring at elevated temperatures in most cases only partially express the truth.

The book is intended as a text-book for students commencing the study of Metallurgy, and as a small hand-book of reference. It has been written in as popular a style as the subject permits, to make it available for the general reader.

The author wishes to express his indebtedness to Messrs. Fraser and Chalmers for several of the diagrams in the chapters on Gold and Silver; and to his former students, Mr. W. H. Mortimore, for Figs. 102 and 106; Mr. Jno. Allan and Mr. W. McD. Malt for assistance in correcting the later proofs.

MANCHESTER,
August, 1895.

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METALLURGY

INTRODUCTION

THE science of Metallurgy deals with the properties of metals in the different conditions they may assume—the changes in these properties induced by the treatment to which they are subjected, or brought about by the influence of other substances with which they may be mixed, either as impurities or for some useful purpose. It also treats of the methods by which they are extracted, in a more or less pure state, from the substances in which they occur naturally, and the refining of the crude products.

The properties on which the usefulness of a metal depends are: specific gravity, elasticity, tenacity, toughness, malleability, ductility, hardness, expansion by heat, fusibility, resistance to atmospheric and chemical action, conductivity for electricity and heat, and the manner in which it affects the properties of metals with which it may be mixed.

The high specific gravity of gold reduces coins of considerable value to a reasonable size, while the low specific gravity of iron, compared with its strength, reduces the weight of iron structures. The cheaper extensive production of aluminium and magnesium by electrolytic methods has led to the introduction of an important series of light strong alloys. The low specific gravity of duralumin and other aluminium and magnesium alloys combined with their strength, workability and reliability when properly treated—age hardened—has made possible many things that otherwise would have been unattainable both in aviation and other fields of activity.

The hardness of steel fits it for cutting-instruments. The elasticity, toughness, malleability, ductility, and tenacity of a metal determine its workability and general usefulness for structural and constructive purposes; the fusibility and expansibility its suitableness for making castings; while a greater or less resistance to atmospheric corrosion is necessary for the general application of the metal.

Useful Metals.—Of the elements classed as metals by the chemist, only some twenty-five occur in such quantity, or possess properties which raise them to such importance, as to be of consequence to the metallurgist. These are—

Iron	Antimony	Manganese	Nickel	Tungsten
Copper	Gold	Bismuth	Cobalt	Vanadium
Zinc	Silver	Chromium	Cadmium	Molybdenum
Tin	Platinum	Mercury	Sodium	Iridium
Lead	Aluminium	Magnesium	Potassium	Tantalum

Rhodium is being used in plating and palladium in leaf. Calcium is being employed in the purification or toughening of lead, copper and other metals.

CHAPTER I

PHYSICAL PROPERTIES OF METAL

Specific Gravity, or comparative density, is the weight of the metal, bulk for bulk, compared with water. It is generally increased by mechanical treatment, such as hammering and rolling.

TABLE OF SPECIFIC GRAVITIES

Water = 1.

Magnesium	1·74	Nickel	8·8
Aluminium	2·56	Bismuth	9·2
Antimony	6·7	Silver	10·5
Zinc	7·1	Lead	11·36
Tin	7·2	Mercury	13·6
Iron	7·8	Gold	19·3
Copper	8·6	Platinum	21·5

Hardness.—This property is very much affected by the purity of the metal and the treatment which it has undergone. Speaking generally, the hardness of a metal—with few exceptions—is increased by the presence of impurities. Gold for coinage is hardened by 8·33 per cent. of copper, and the presence of a small percentage of carbon in iron converts it into steel. Other examples will be found in the text. By suitable heat treatment, steel may be made hard enough to scratch glass, or soft enough to be turned and worked freely. (See Tempering Steel.) Mechanical treatment, such as hammering, wire-drawing, rolling, and pressure in the cold state, hardens metals—work-hardening. In this manner the bronze weapons of the ancients were hardened. Annealing—heating to redness and allowing to cool very slowly—generally has the effect of softening the metal. In the case of copper this is reversed, rapid cooling, such as quenching in water, softening that metal and many of its alloys. Metals are usually softer when hot than when cold.

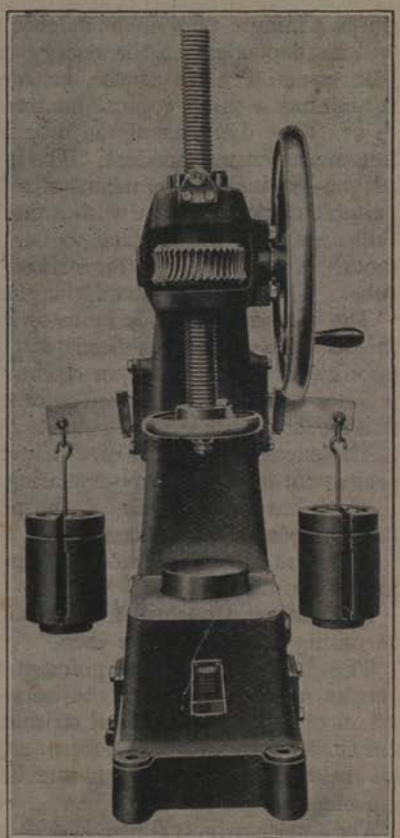
Hardness is determined relatively by comparison with other bodies of standard hardness. **Mohs'** scale of hardness, first used for minerals, consists of the following substances: 1 talc, 2 gypsum, 3 calcite, 4 fluor-spar, 5 apatite, 6 felspar (orthoclase), 7 quartz, 8 topaz, 9 sapphire, 10 diamond. Comparison is made by scratching the surface. **Turner's Sclerometer** has a jewelled point that can be weighted till a movement over the surface of the metal produces a scratch of standard depth.

This is probably the nearest approach to an absolute method, but only deals with the exposed surface.

Hardness Tests.—For practical purposes three methods are in

common use for the determination of this property. Neither is absolute, but they provide the engineer and user of the metal with useful information which he can utilise in the manipulation or application of the metal.

The Brinell hardness test consists of indenting the smooth surface of the metal by a hardened steel ball—usually 10 mm. in diameter—by subjecting it to a pressure of 300 kilograms for soft and 3,000 kilograms for harder metals. The diameter of the indentation is measured by means of a micrometer microscope and is used as a basis for calculating comparative figures—hardness numbers. For very hard materials a 2 mm. diamond ball is employed.



Messrs. Avery, Ltd.]

FIG. 1.—Brinell Hardness Machine.

The standard **Brinell** machine is shown in Fig. 1. Pressure, however obtained, must be steadily applied and maintained for a definite time. The maximum is attained in about 10–30 seconds.

The hard steel ball is carried in a socket at the end of the screw pillar, which can be adjusted for height to accommodate materials and test pieces of varying thickness. Provision is made to balance the weight of the test piece, so that the full pressure is exerted.

The pressure is applied by the screw through the worm wheel, and is maintained for 15 seconds in the case of hard materials and 30 seconds for softer materials. In the machine shown the load is actually weighed. The pressure exerted on the platform on which the material rests, acts through a system of levers similar to those on a platform weighing-machine and is increased till the weights are lifted. Special types of machine operating on the same principle for use on hard materials, thin sections, case-hardened surfaces, or of special shape for particular purposes using balls of smaller diameter or balls of diamond and using different loads, are also in use. The pressures employed vary, but the hardness

figures are calculated as before, either from the diameter of the impression or on the depth of penetration.

The **Shore Scleroscope** for hardness testing is a "rebound" instrument in which a small conical hammer with a blunt point, falling freely by gravity, strikes the surface of the metal and rebounds. If the hammer falls always from the same height, the energy in the blow it strikes on falling will be constant. The hammer-blow produces a minute permanent indentation and the height of the rebound will be dependent on the energy unabsorbed by the material struck. The essential parts of the instrument are a graduated glass tube containing a small conical hammer with a diamond point weighing $\frac{1}{12}$ oz. The diameter of the tube is 0·002–0·003 inch wider than the hammer to ensure freedom. The hammer is drawn up to the standard height—10 inches—by means of a bulb and locked in position by a suitable device provided with a pneumatic release. When released it falls freely on the surface to be tested, suitably fixed at the open mouth of the tube. After striking the material it rebounds up the tube. The height is noted, the graduations reading from 0 to 140.

The diamond point is more or less spherical, the striking surface measuring 0·02 inch in diameter. The force of the blow is equal to approximately 220 tons per sq. in.

Since the indentations are so minute they do not affect the surface, and finished work can be tested without damage.

The successful action of the instrument depends on producing a permanent indentation representing the work absorbed.

Work hardening occurs at the point of contact, so that tests must not be repeated on the same spot.

Standard blocks 100° and 40° hardness are used to check the instrument from time to time.

Herbert's Pendulum Tester, shown in Fig. 2, is rapidly becoming more generally used.

The diamond spherical point at the lower end of the central post acts as a pivot on which the horseshoe weight rests in equilibrium. When one side is depressed on release it moves as a pendulum, and the time of the swing is determined by the depth of the impression on the material. Owing to the balanced nature of the weight the movement is slow.

The time hardness figure is deduced from the time occupied by ten single swings of the pendulum.

As the impressions are very small this instrument can be applied to finished work. Special devices are provided to enable a horizontal surface to be ensured for the point to rest upon.

Age Hardening.[1]—When certain alloys, especially certain aluminium-copper silicon and aluminium-magnesium alloys containing silicon and iron, are left at room temperature for a considerable time after quenching they become harder and stronger. This effect is

[1] Hardening and Tempering, see p. 179.

hastened by annealing at 130°–150° C. Duralumin and other alloys are thus treated to develop the best mechanical properties. Changes in the microscopic structure are responsible for the developments that occur.

In all methods of testing hardness other properties of the metal are involved and influence the result. Wearing hardness is quite different and is measured in other ways, mainly by abrasion or rotating contact. Reduction in size or loss in weight of the metal are used as the basis of comparison.

Machinability depends on many factors of which hardness is one. For practical purposes, drilling or turning tests on standard prepared specimens are employed.

Courtesy Messrs. Ed. G. Herbert, Ltd.]

FIG. 2.—Herbert's Pendulum Tester.

In every case factors other than simple hardness influence the result.

The physical, and to some extent probably the chemical, behaviour of a metal is dependent upon its internal structure. Formerly the fracture presented by the metal was the only means of gaining any clue to the structure of a metal. This at best, could only furnish a very rough indication. The adoption of microscopic examination has provided the means of more accurately investigating the structure, while the later applications of X-ray examination, as applied to metals, have enabled the molecular arrangements to be studied. Both methods of investigation also have put into the hands of the metallurgist means for ascertaining the distribution of components, and the presence of cavities, inclusions, lack of homogeneity, and other

faults in the material, as well as the changes that may occur in distribution and in structure induced by heat or mechanical treatment or during the working life of the material.

Metals are generally obtained in or reduced to a state of fusion. Wrought iron and some of the electro-deposited metals are exceptions.

Like other fluids, metals on solidifying usually assume a crystalline condition. If the conditions allow, the crystals may be easily recognised owing to the production of a more or less definite geometrical form.

FIG. 3.—Crystal of iron from a steel ingot.

Fig. 3 shows such a crystal from an ingot of steel. Fig. 4 shows crystals of lead.

Such crystals are formed when the solidification takes place by cooling from the outside, under conditions which favour rapid or fairly rapid removal of heat from the external surface.

FIG. 4.—Crystallised lead.

Note.—All metals have definite latent heats of solidification. See page 16. When the metal cools throughout its mass to its melting-point before solidification commences, crystallisation may begin anywhere in the interior. It commences at many centres from which the crystallising tendency radiates and proceeds spherically until the spheres of influence come into contact, then extends till the liquid included between the spherules is appropriated, producing polygonal forms, which resemble spheres compressed till the surfaces are brought into contact. See Fig. 5, pure gold.

Like other crystallising bodies metals tend to become purer by rejecting other substances which may be present either as impurities or in admixture. Thus the crystal from the steel ingot shown in Fig. 3 was nearly pure iron. Other examples may be found in Pattinson and Parke's processes. See lead, pp. 250, 253.

The rejected bodies may form inclusions and be entangled in the metal, interfering with the homogeneity of its structure, or, if the metal be quite liquid, may rise to the surface if there is a difference in specific gravity, *e.g.* Kish, see p. 145.

In alloys the constituent metals may solidify together as a solid solution, see below.

Fig. 6 shows a micro-photograph of copper containing lead, Fig. 7 a micro-photograph of steel showing a segregation of sulphides.

Where the case is one of simple segregation of an impurity or a compound, its effect on the properties will be limited to the extent to which it interferes with the continuity of the structure and the contingent circumstances arising therefrom.

In many cases, however, other considerations arise. Molten metals follow the same laws as other liquids. They act as solvents, and their solvent power varies with the temperature, so that they may retain

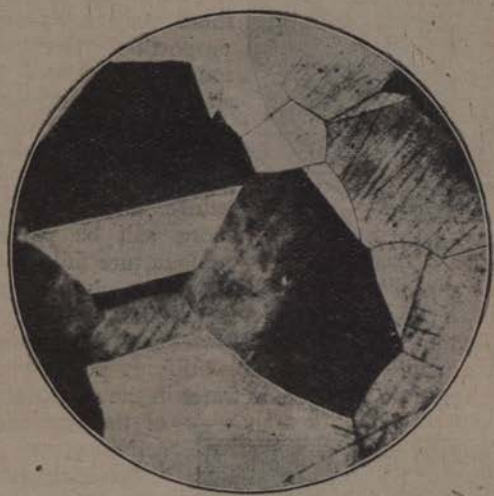


FIG. 5.—Photo-micrograph. Pure gold.

larger or smaller amounts of other metals in solution as the temperature rises and falls. In making castings this may have far-reaching effects. The hot, fluid metal may be perfectly mixed and its components in solution, but in the course of solidification more or less complete separation may occur.

When substances are mixed together in solution, the melting and solidifying points are often lower than the mean melting-point of the mixture, and often below the melting-point of the more easily fusible constituent. Thus, an alloy of 2 parts of potassium, melting-point 62·5° C., with 1 part sodium, melting-point 99·6° C., remains quite fluid at the ordinary temperature and runs like mercury. (The alloy may be made by melting the metals together under heavy petroleum.)

In all cases, however, there is an alloy containing certain proportions of the metal having a lower melting-point than any other mixture of the metals. This alloy solidifies at a definite temperature, and

represents the mutually maximum proportions with the lowest melting-point.

During solidification molten alloys and impure metals behave more or less like other solutions, and the solidifying point (melting and freezing points) may be depressed by the presence of dissolved metals or impurities in the same manner as other liquids carrying dissolved solids, *e.g.* water and salt, the depression being dependent on the amount of substance in solution, and there may be a limit to the proportions that can remain mutually dissolved in the fluid state at any temperature.

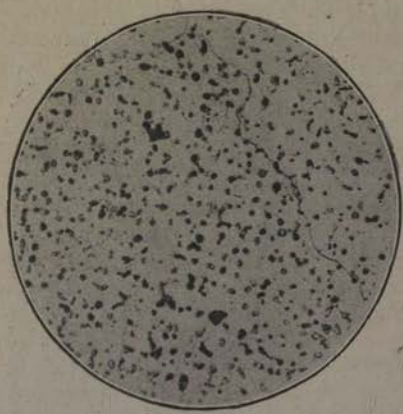


FIG. 6.—Lead in copper.

With salt and water the proportions are water 77·6 per cent. and salt 22·4 and the temperature minimum −21·2° C. If more salt be present, as the temperature falls it separates as a solid till the proportion has fallen to 22·4, and the temperature to −21·2, but if less, ice separates till that proportion has been reached. If the temperature falls below −21·2° C., the still remaining liquid solidifies completely, *i.e.* the solidifying point of the mixture is −21·2° C. As salt is insoluble in water in the solid state separation of the two occurs during solidification.

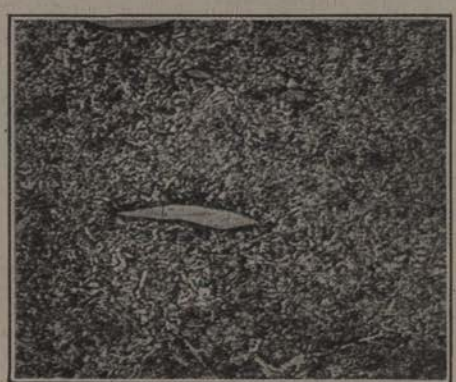


FIG. 7.—Sulphide segregation in steel.

Similarly, with a mixture of molten metals, as the temperature falls, portions may solidify leaving the still liquid portion richer in that constituent which will produce an alloy of a lower melting-point, until the proportion is reached which has the minimum melting-point, and solidification is then completed, without a further fall in temperature, as the heat is dissipated. Some metals, however, are capable of remaining in solution in the solid state to a greater or less extent, and the portions that solidify in such cases are not pure metals.

It will depend on the proportions in which they are mixed whether

the mixture of lowest melting-point is produced. It will only be produced when the proportions exceed the limit of solid solubility at the melting-point of the most fusible mixture.

The portion to solidify last must, of course, lie mainly outside and envelop the portions already solid, and thus be moulded on the crystals and crystallites formed or in course of formation, thus producing a greater or less break in the continuity of the structure with a corresponding effect on the properties, depending on the character of the separated matter. The alloy or mixture having the lowest melting-point in a series, and which during solidification remains fluid longest, *i.e.* to the lowest temperature, is described as the **eutectic.**

Strictly speaking, the eutectic of a series should have a definite composition when molten, but separation of its components will take place when it solidifies. Components may not mean elements or compounds. Thus the homogeneity of the structure may be broken in quite a natural manner with corresponding effects on the physical properties.

It does not follow that pure metals will separate in the course of solidification of alloys. In the crystallisation of chemical compounds many salts retain a portion of the water in which they were dissolved as water of crystallisation, and the amount so retained may be varied. These variations are accompanied by changes in form or properties. So also may the solvent and solute in a solidifying mixture of metals produce mixtures of varying composition, but which may attain a crystalline condition if not a definite form, the amount of each constituent varying with the conditions of temperature and perhaps pressure. Such mixtures may present no definite atomic ratios, but the body so separating may be sensibly homogeneous. It is usual to describe such bodies as "solid solutions." Thus the α solution of brass (copper and zinc) may vary from 100 per cent. copper to 70 per cent. copper at the moment of complete solidification and to 63·5 per cent. at the ordinary temperature. Any alloy within these limits will present a uniform structure when microscopically examined. (See Fig. 8.) There may be, however, certain variations in appearance within the crystal grains of a more or less regular type. These result from the tendency, as the temperature of the molten metal falls, for a solution to solidify containing a larger amount of copper—the body of higher melting-point—than the average proportion in the mixture, leaving the portion still fluid richer in zinc. During the progress of the solidification interchange of constituents between the fluid and solid portions, which results in the establishment of an almost uniform composition within the grain, may take place, but this may be incomplete, and the crystallites first formed may not be obliterated. The irregularities in the individual grains arising from this cause are described as "coring."

In brass several solid solutions of fixed limiting proportions exist. Fig. 9 shows the γ solid solution. It contains 40 per cent. of copper. Compare pure gold, Fig. 5.

From the foregoing it will be seen that from the beginning of its existence as a solid a metallic mass may possess a more or less complicated structure varying from the simple one-constituent structure of pure metal, or simple solid solution without coring, to the complex structure arising from (*a*) the presence of foreign bodies as inclusions (slag, etc.), (*b*) segregated impurities, (*c*) the separation and presence of different solid solutions (see Fig. 10) containing differing proportions of the metals present, and (*d*) the formation and separation of a eutectic.

FIG. 8.—*a*. Brass, showing similar character of grains.

These can be detected by microscopic examination, and the conditions under which they form and separate determined in various ways.

Fig. 11 is a photo-micrograph of white bearing metal showing three constituents.

Changes in the Solid Material.—Changes in composition of the components and in the distribution of the constituents may take place in the solid state when the conditions are favourable. The components—metals, metallic compounds, or solutions—may diffuse as the temperature is

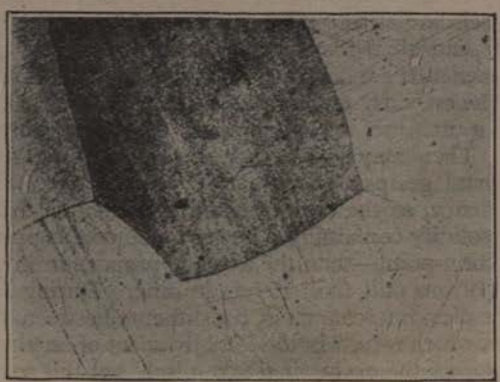


FIG. 9.—*γ*. Brass, showing complete solid solution.

raised, even below the melting-point, and again separate as the temperature falls, unless separation is prevented by quenching and cooling so rapidly as to prevent the free movement of the molecules and arrest them in the condition they had at the moment of quenching.

FIG. 10.—α and β. Brass.

FIG. 11.—White bearing metal showing three constituents.

Figs. 12, 13, show a steel casting as cast and after annealing, Figs. 14, 15, a piece of tool steel in its ordinary soft condition and after heating to redness and quenching from a red heat. In the former case the redistribution of the carbon compound will be noted, and in the latter that the quenching has prevented the separation of the white constituent—Fe_3C, cementite.

From the foregoing it will be observed that internal structure is not merely dependent upon the composition of the metal—except in the case of pure metals—but upon many other things, and that the physical properties may vary within wide limits and be determined by the internal character of the metal.

FIGS. 12, 13.—Steel casting before and after annealing.

All the effects of mechanical treatment must be considered in the light of these facts, since they have great influence on the distribution of force within the mass. Coker has shown[1] that the effect of holes and other variations of form in solids is to produce a large concentration of force in the neighbourhood of the hole, and the effect of a nick in so concentrating force as to make it easy to break a bar of metal is well known. The variations, inclusions, and irregularities which cause a break in the continuity of the structure have corresponding effects and are responsible for much, if not all, of the deterioration in mechanical strength which sometimes occurs in metal during its working life. The repeated application of stresses too small to produce fracture may, as the result of such concentration, institute or extend internal incipient fractures or otherwise weaken the metal below its normal working load.

A rough idea of the internal character of the metal may be obtained from the fracture.

[1] *Trans. Inst. Engineers and Shipbuilders*, Scotland. 1919–1920. lxiii. 34–94.

FIG. 14.—Tool steel slowly cooled.

FIG. 15.—Tool steel quenched.

Fracture is the appearance presented by metals when freshly ruptured.

Metallic fractures may be classified as—

Crystalline.—Metals presenting this appearance are weak. Fracture occurs by the separation of the adherent facets or by cleavage. Antimony, bismuth, and zinc offer good examples of this kind of fracture.

Granular.—This fracture presents the structure of a sandstone. The uniformity of the mass is greater than when crystalline, and the metal is consequently stronger and more readily worked. Cast iron is a good example of this structure.

Fibrous.—This structure is developed to the greatest degree in wrought iron by the elongation and welding together of the particles during rolling. The toughness and strength of this metal are well known.

Silky.—This is a finely fibrous fracture of brilliant silky lustre. It is best seen in copper and steel. Metals which possess it are usually strong, tough, and malleable.

Conchoidal.—This appearance is presented by the harder varieties of steel. The metal breaks with a convex or concave surface with divergent markings somewhat resembling a shell. Metals possessing this fracture are usually hard, highly elastic, and brittle.

Columnar.—The columnar structure is manifested by the tendency of the metal to separate in long fingers across the thickness of the cake or ingot, the pieces somewhat resembling lump starch. In tin it may be obtained by heating the metal nearly to its melting-point, and then either allowing it to fall on the ground, or by striking it sharply with a wooden mallet while hot. It is a very unsatisfactory fracture.

The fracture of a metal varies with the purity, temperature, and manner in which the rupture has been produced: *e.g.* wrought iron containing phosphorus breaks with a crystalline fracture; copper at a full red heat breaks with a coarsely granular fracture; while wrought iron, if nicked *all round* and broken short off, may present a granular fracture, but if nicked on one side only, and then bent over and broken, it exhibits a fibrous fracture.

Fusibility.—All metals, with greater or less difficulty, have been reduced to a fluid condition by heat. The readiness with which this can be done and the temperatures required to effect it vary greatly. Tin, lead, and zinc melt in an ordinary fire, platinum only in the oxy-hydrogen blow-pipe flame. Many metals, before fusing, pass through a soft, pasty stage, *e.g.* iron and platinum; others pass directly from the solid to the liquid state. This applies to alloys also. The alloy of two parts lead and one part tin, used by plumbers to make the joints of lead pipes, is an excellent instance of this, the knob of metal round the pipe being wiped on and shaped with the metal in the pasty state. This is due to the separation of solid lead in the cooling alloy leaving a fluid portion richer in tin and having a lower melting-point. See p. 369.

Most metals contract on solidifying and are denser in the solid state. Bismuth is an exception. Its density in the liquid state is 10·004 and 9·673 when solid.[1] Cast iron is another apparent anomaly, but this is due to the separation while solidifying of carbon, which has a lower density and increases the volume. See p. 146.

Metals which do not become pasty, and which expand on solidifying, bring out finer impressions of moulds when used for making castings. Certain qualities of iron are consequently superior for this purpose, and for a similar reason bismuth is added to zinc and tin alloys, for casting the so-called artificial "bronzes," and for making alloys for patterns.

[1] This corresponds with a linear expansion of 0·014 and a cubic expansion of 0·0342.

The fluidity of metals when melted is very variable. For casting purposes, the metal must flow freely, or portions of the mould will not be filled—cold shorts—and the sharpness will be destroyed.

When metals are mixed together to form alloys, the melting-point of the mixture is lowered, sometimes in a remarkable degree, even below the melting-point of the most fusible constituent, *e.g.* a mixture of 1 lead, 1 tin, 2 bismuth melts in boiling water. (For melting-points of tin and lead alloys, see p. 343.) This is taken advantage of in the production of the so-called "fusible alloys," which are required to melt at a certain temperature, and for solders. Alloys used for the latter purpose must melt more readily than the objects to be soldered.

TABLE OF MELTING-POINTS.

Tin	232° C.	Copper in a reducing atmosphere	1084° C.
Bismuth	268°	Gold	1064°
Lead	327°	Cast-iron	1200-1350°
Zinc	419°	Nickel	1452°
Antimony	632°	Iron	1503°
Aluminium	657°	Platinum	1755°
Magnesium	651°	Iridium	2454°
Silver in air	955°	Tantalum	2850°
Silver in a reducing atmosphere	962°	Tungsten	3267°
Copper in air	1062°		

Latent Heat.—When metals or other substances change their state, a definite quantity of heat is required to effect the change from solid to liquid or to gas, or is evolved in passing from gas to liquid or solid. The heat thus absorbed or evolved during the change does not affect the temperature which remains stationary till the change is completed. Thus in melting ice the thermometer remains at 0° C. till the whole is melted, and in freezing water the temperature does not fall below 0° till all the water is frozen. The heat thus absorbed or liberated which does not affect the thermometer or other instrument is described as latent heat.

A pound of ice at 0° C. absorbs 79 units of heat in producing a pound of water at 0° C. A pound of water at 100° C. (the boiling-point of water) absorbs 537 heat units in passing to a pound of steam at 100° C.

Metals behave similarly. In melting each metal absorbs a definite amount of heat and on solidifying this heat is liberated. Similarly, on volatilising heat is absorbed and is liberated on condensation.

The amount of heat thus absorbed affects the rate of melting. For the same heat exchange conditions it will be faster or slower, dependent on the quantity of heat passing.

Similarly, in cooling, the larger the quantity of heat evolved, the time taken to completely solidify will be more prolonged.

This may have far-reaching effects on the structure of alloys and on castings, the heat having to be conducted away by the material of the mould.

These facts have in recent years been largely applied in influencing the shape, material and method of cooling the moulds in making

ingots, with a view to prevent segregation and variations in composition or structure. In some cases water-cooling of moulds is resorted to. See alloys, p. 338.

Other effects connected with the contraction of the metal on solidification and cooling are also affected by the latent heat of a metal (p. 146).

Note.—For definition of heat unit, see p. 67.

LATENT HEATS OF FUSION.[1]

	Temp. °C.	Heat cal/g.
Ice	0	79·24
Aluminium	658	92·4
Bismuth	268	12·64
Cadmium	320·7	13·66
Copper	1083	50·0
Iron, grey-cast	—	23·0
,, white-cast	—	33·0
,, slag	—	50·0
Lead	327	5·86
Mercury	−39	2·82
Nickel	—	4·64
Palladium	1545	36·3
Platinum	1755	27·2
Silver	961	21·7
Sodium	97	31·7
Tin	232	14·0
Zinc	419	24·09

Expansibility.—The amount by which a metal expands and contracts on heating and cooling greatly influences its value for making castings. Apart from the difficulties arising from the presence of cores—that is, parts of the mould surrounded by the metal and which by offering resistance to the contracting metal might produce fracture—the variations in thickness in the different parts of the casting will tend to cause different parts of the same casting to cool at different rates and contract unequally, thus setting up stresses which may produce fracture, or, failing that, to set up internal stresses which greatly weaken the casting. For casting purposes a metal with minimum contraction would serve best. In grey cast-iron the carbon which separates during the solidification largely counteracts the contraction due to cooling, and thus renders it easier to produce complicated castings, and sharply-defined castings of an ornamental character.

Volatility.—Some metals are readily converted into vapour by heat, and are described as volatile metals. Such metals can be distilled, the vapour being led into condensers and cooled. Mercury, zinc, cadmium, sodium, potassium, and arsenic are obtained from their

[1] Hodgman, Coolbaugh and Senseman's "Handbook of Chemistry and Physics."

ores in this way, the vapour of the reduced metal being led away from the reduction chambers, or retorts, and condensed.

Note.—Volatility is only a relative quantity. Almost all metals are volatilised to a greater or less extent at very high temperatures, such as are obtainable in the electric arc and furnace, while lead, antimony, gold, and silver are sensibly volatile at furnace temperatures.

Tenacity.—Resistance to fracture by a stretching force is possessed by all metals in a greater or less degree. It is expressed by the maximum dead weight which a bar of given sectional area can support without rupture. In English measures it is expressed as the number of pounds or tons supported by a bar one square inch in section; in metric measure, as kilogrammes per square millimetre or centimetre.

TABLE OF RELATIVE TENACITIES.

Steel	100	Gold	12
Wrought Iron	30–40	Zinc	2
Cast Iron	10–24	Tin	1–3
Wrought Copper	18–20	Bismuth	1–1·5
Cast Copper	12–25	Lead	1
Cast Silver	25	Lead (wire)	1·5–2·5
Aluminium	20–28	Antimony	0·8

The steel taken as 100 has a tenacity of 60 tons per square inch.

This property is greatly affected by the purity, structure, temperature and treatment the metal has received. Certain impurities in some cases may increase the tenacity and in others diminish it. The conditions in which the impurity exists, whether in combination or solution, or in the free state, is also important. The small amount of carbon—existing as carbide—in iron necessary to convert it into steel raises the tenacity, the larger amount in cast iron reduces it, the actual effect depending on the manner in which it occurs—free or combined. The effects of structure have been referred to, see p. 12.

Speaking generally, tenacity is reduced by marked increase in temperature. Mild steel used for structural work (28–30 tons tensile) shows a slight increase from 150° C. to 250° C.; but falls on further heating. At 600° C. it is approximately $\frac{1}{3}$, and at 950° C. less than $\frac{1}{5}$ of its normal strength. Cast iron is unaffected to 500° C. At 950° C. it is about $\frac{1}{5}$ normal. Other metals are variously affected.

Conversely, exposure to low temperatures such as liquid air raises the tenacity. The tensile strength of cupronickel is raised 50 per cent., red brass, 40 per cent., yellow brass, 30 per cent. Solder disintegrates, due to the production of grey tin. See p. 306.

The treatment a metal receives may be of various kinds, mechanical, heat, or chemical. Malleable and ductile metals subjected to mechanical treatment, such as hammering, rolling, wire-drawing or otherwise stressing, especially in the unheated state—cold working—are generally stronger than cast specimens of the same metal. This is utilised in producing strong sections for special purposes. Thus a steel wire drawn to No. 14 gauge—0·087 inch in diameter—from a bar with a T.S. of 57 tons had a tensile strength

of 98 tons. This increase in strength—and hardness—is largely due to structural changes resulting from the mechanical deformation of the original structure. This is most pronounced on the outside. The tensile strength of the interior is not raised to the same extent, as may be proved by removing the outer layers.

The increase in hardness and strength is reduced or entirely removed by heating the metal to full redness or other suitable temperature and allowing it to cool slowly—**annealing.** This also restores the malleability.

Effects of Heat Treatment.—As will be seen (Figs. 12 and 13, p. 12), the structure of metals is greatly influenced by the heat treatment they receive. This may vary in temperature, time of exposure, and rates of heating and cooling. All these have their influence on the tenacity and other mechanical properties of the metal. Much of the advance that has been made in modern metallurgical practice, especially in the direction of engineering requirements, depends on the changes so induced. Formerly, only steel was considered in this connection, the hardness, elasticity and other properties being modified to suit requirements by heat treatment in hardening and tempering. In modern practice many metals and alloys are heat treated, most metals, in fact, being susceptible to improvement by approved methods. This has been specially developed in aluminium and nickel alloys.

Annealing, tempering, general heat treatment, and age hardening are all examples of such processes. Temperature and time determining the intensity and duration of the treatment and the rate of cooling all influence the final result. The results are generally due to the effect of heat or the rate of cooling on the solution or separation of some constituent in the solid state (as in the case of steel, see p. 179), or on the grain size of the metal. Speaking generally, larger grain size is associated with weaker material, hence treatment may be given to refine the grain, as in case hardening (see p. 189) and other processes.

In age hardening duralumin the separation from the metal of certain compounds accompanies the increase in strength. See p. 4.

Chemical Effects.—These include atmospheric and other corrosion and also treatment which may be resorted to for removal of scale, or cleaning for coating with other metals, as in galvanising and plating. Changes brought about by such treatments reduce the tensile strength, sometimes to a phenomenal extent. The action may be intergranular —beginning at the joints of the crystal grains at the surface and extending inwards. In extreme cases, as in the caustic embrittlement of steel, actual cracks may develop and the tenacity be reduced practically to zero.

In pickling in acid to remove scale and oxide a considerable falling-off may occur, possibly due partly to occluded gas generated by the action of the acid on the metal.

Atmospheric corrosion, beside reducing the cross-section of the

metal, may also produce weakening by intergranular attack, beginning at the surface. The effects of chemical action must always be considered in the light of stress distribution and concentration, noted on p. 12.

The tenacity of a metal often changes as the result of the situation in which it is employed. Iron and steel frequently become apparently crystalline and brittle by continued vibration or by frequent heating to redness and cooling, and are in consequence weakened. Many accidental fractures result from this cause.

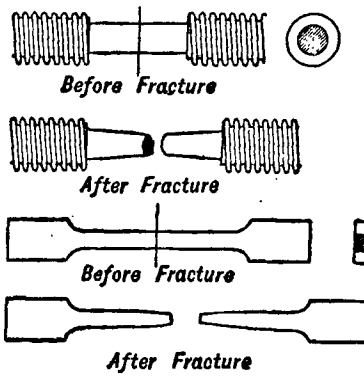


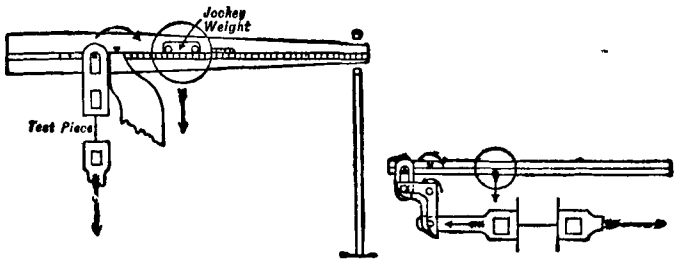
FIG. 16.

Determination of Tenacity.—Tenacity is determined by straining a piece of the metal of known dimensions and observing the amount of force required to break it.

For this purpose a test piece of the metal is prepared of a form suitable for the machine to be employed. These may have ends shaped to fit the grips of the machine, screwed, collared or shouldered, and be round, flat, or of other shape as required.

Fig. 16 shows test pieces before and after breaking.

The ends of the piece are securely held and the jaws gradually forced apart by mechanical or hydraulic power until the maximum load required to break the test piece is attained. The force required is weighed by a simple or compound lever arrangement (Figs. 17, 18),



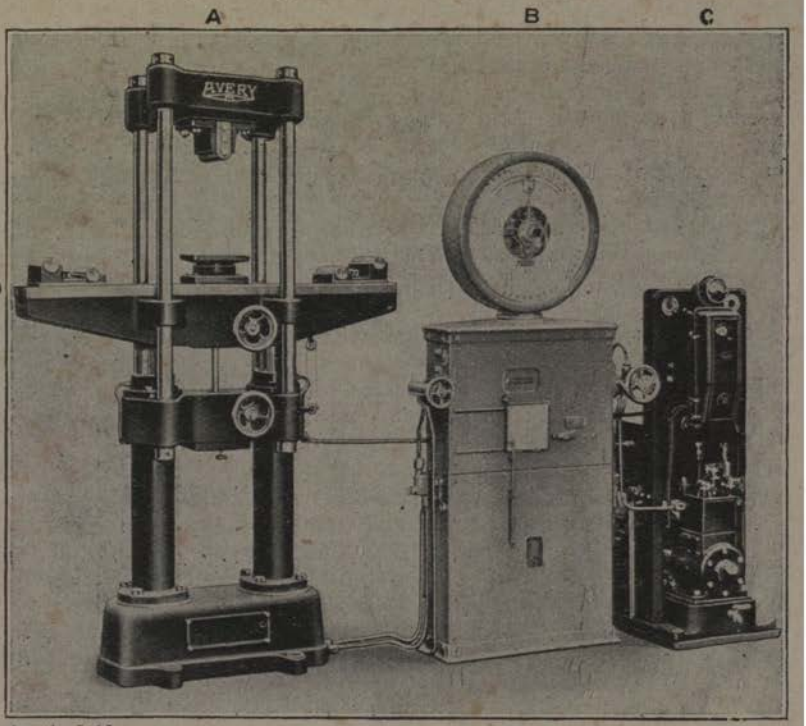
FIGS. 17, 18.

or instead of weighing the force, gauges are employed to register the pressure and the force calculated.

The force required to fracture a piece is generally greater if applied at once than if gradually applied.

Modern testing machines are often designed for making a variety of tests—tensile, compression, transverse, bending and shearing, and sometimes torsional in the same machine.

The Avery self-indicating universal machine shown in Fig. 19 is of this class. The strain is applied by oil pressure (elaulic). The main pressure cylinders on the straining unit A are connected with a small hydraulic cylinder in the measuring and control unit B. The sectional area of the ram of this cylinder bears a definite ratio to the total area



Avery's, Ltd.]

FIG. 19.—Universal Testing Machine.

The straining unit A consists of a moving platform operated by oil rams at the side and moving between two massive fixed heads, under and above it. The grips for tensile tests are in the lower head and the centre of the moving platform D, the top of which carries a table and rests for making transverse bending and compression tests between it and the fixed top of the unit. The operating unit C consists of an electrically driven oil pump.

of the rams of the straining cylinders, thus effecting a proportional reduction of the total pressure. This fraction of the pressure acting on the small ram operates on a system of compound reduction levers which finally operate the dial mechanism which is provided with an indicating device.

Provision is made for controlling the rate of application of the load or to maintain it stationary for the taking of extensometer readings.

Suitable provision is made to eliminate friction of the small ram and also shock when the test piece gives way.

This machine is calibrated by dead weight reading, the graduations reading to approximately 0·2 to 0·25 per cent. of the total load capacity.

Its working capacity can be changed by a lever, and separate dial graduations are provided for high and low capacity working.

In making tests, whether for tenacity or resistance to compression, the behaviour of the test piece during the operation is equally as important as the total load.

Elasticity.—It will be observed that the specimens after testing are longer than before.

If during a test the strain on the test piece be relieved at intervals by removing the load it will be found that the test piece has retained or returned to its original dimensions. When a certain strain has been exceeded the recovery is not complete. The material has acquired a permanent set. The elastic limit has been exceeded. The accurate determination of this point can only be made on specially prepared specimens with delicate instruments, while the delays necessary very much prolong the operation.

Up to this point material is only subject to elastic deformation. The maximum amount of force that may be applied without permanent deformation marks the elastic limit.

When the extension (strain) ceases to be proportional to the stretching force (stress) permanent changes occur, and actual movement within the metal takes place. This deformation is the result of plastic flow.

Determination of the point at which this becomes sensible is easily observed with many elastic metals and is noted when making the test. In such metals at a point a little beyond the elastic limit a sudden movement of the indicator marks the elongation that occurs. This is noted and is known as the yield point. Bronzes and most copper alloys do not show this point. Its occurrence is definitely marked on the indicator chart, while the elastic limit can only be ascertained by prolonged and repeated tests. The ratio this bears to the ultimate strength of the material is taken as a measure of its resistance to changes in form and structure in actual use. A high "yield" point is demanded for materials subject to variations of stress such as shafts and moving parts of machines. There should, however, be always such a margin between this force and the tensile strength as to remove the material from the region of brittleness.

Fig. 20 shows charts from simple lever machines. They indicate the movement in the test piece during the test.

The extension of the material is accompanied by a reduction in area and also work hardening, which almost always accompanies molecular or plastic movement of the material. This is most marked in the cold. In heated materials self-annealing takes place as the work is done and hence it may not be apparent in the final product. The temperature at which this takes place varies with different

metals, and depends on the stress necessary to produce deformation. Thus lead anneals on warming, while steels require intense and prolonged heating to permit of the movement of the particles into relatively natural positions from which they have been forced.

Elongation.—The amount of extension that occurs before fracture is to some extent a register of the ductility and toughness of the metal. At any rate, it provides some evidence of the working properties of the metal. This must, however, be considered in conjunction with the sectional area of the test piece at the point of fracture.

Usually up to the yield point extension occurs uniformly over the whole length of the test piece. Later much of it is confined to a portion or portions which elongate more rapidly, the sectional area

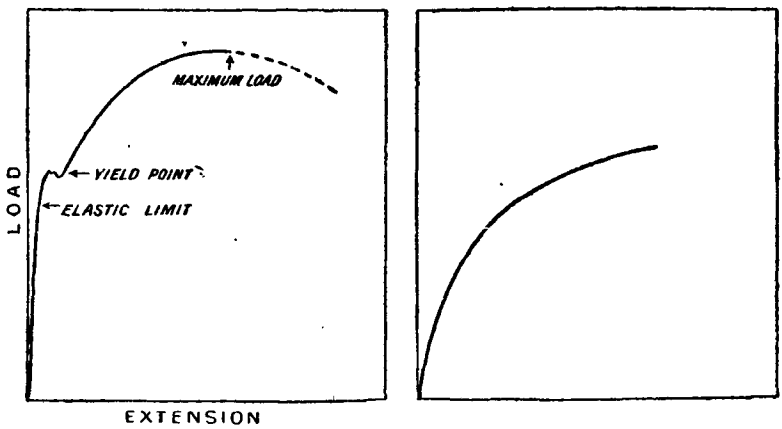


FIG. 20.

at such points being considerably reduced. This " necking " of the test piece may represent a large proportion of the total elongation and vitiate or largely influence inferences drawn from the facts.

For this reason it is important to specify lengths of test pieces and also the sectional area, also the position of the centre pop marks between which measurement is taken.

Note.—In one case it was found that a competing firm were using 12-inch test pieces marked in inches and measuring the final length (for comparison) between the three marks containing the fracture wherever it occurred.

In the absence of a recording appliance on the machine, indication of the attainment of the yield point can be made by means of compasses (dividers) set to a definite length and applied between marks on the chalked surface of the test piece as the test proceeds. Final measurements are made by putting the broken ends together and using compasses and a rule, and using a micrometer for the diameter or thickness. Results are scheduled.

Dimensions of test piece—

Ultimate strength	tons per square inch
Yield point	,, ,, ,,
Elongation	per cent. of original
Reduction in area	,, ,,

It is highly important that the stress applied shall operate along the axis of the specimen to obviate any bending or other effect. For most materials the grips enable this to occur, adjustment taking place automatically.

The fractured ends of the test piece are carefully examined. The fracture should be symmetrical. In round specimens of homogeneous tough material, such as mild steel, the ideal form is a cup and cone. Fractures are examined for imperfections, which may indicate inclusions or lack of homogeneity. Both interfere with the uniform (in the case of steel—silky) appearance of the fracture and may indicate liability to fatigue or unreliability.

The results on most modern machines can be automatically recorded.

"Creep" is the term given to the gradual extension that occurs in many seemingly rigid materials when subjected to load over long periods of time.

Other tests applied to metals for constructive purposes may be compressive, torsional, bending and transverse tests and fatigue resistance.

Compression tests for metals are usually carried out on cylindrical specimens with a ratio of height to diameter of 2 : 1. Metals of a plastic character show no breakdown point. The tests can be made comparative by stating the force required to reduce the length by a definite proportion—usually 50 per cent. More brittle metals give definite results and figures which enable the results to be used for calculation in design.

Bend tests are always specified on malleable materials such as iron and steel. These may be hot or cold, and in the case of steel may be required on material that has been heated to redness and quenched in water or after other treatment.

Rivets.—Boiler plate and test pieces from most important machinery parts are thus tested. The angle to which it must be bent and the radius of bending when the angle exceeds 90° are stated.

All bends should be examined on the inner as well as on the outside. The middle of the test piece is neutral, but during the test the outside is in tension and is elongated while the inside is in compression and diminishes in length. The freedom with which the metal accommodates itself to both conditions furnishes evidence of its malleability and reliability under ordinary conditions of working. No cracking should occur on either side.

For rivets the shank should bend close on itself and the head hammered out to $2\frac{1}{2}$ times the diameter of the shank. Plates may be bent through 180° on a radius equal to $1\frac{1}{2}$ times their thickness—cold, hot or after quenching.

Test pieces from steel castings are usually only bent through 90°, a test piece 9 × 1 inch square being specified and 9 × $1\frac{1}{4}$ inches with rounded edges of $\frac{1}{10}$ inch radius for forgings. The bending radius for forged material varies with the tensile strength from $1\frac{1}{4}$ inches for 40-45 tons material to $\frac{3}{4}$ inch for material 25-32 tons tensile.

Torsional tests are carried out on material for shafts and other applications likely to produce torque and on wires. One end of the test piece is firmly gripped in a chuck which may be rigid or attached to the weighing apparatus. The other end is held in a chuck capable of being revolved as required. The angle through which the piece is turned is registered and also the load as indicated by the machine. These are plotted, the former as ordinates and the latter as abscissæ.

In wire tests the number of complete twists forms an indication of its toughness. High torsional strength also indicates the probable resistance of steel to many of the accidental causes which frequently lead to fracture.

Fatigue is the gradual deterioration in a metal which may occur under the ordinary conditions to which it is subjected in use. These include changes of temperature, shock, vibration, whether by rotating impulses or other causes.

The possible rearrangement of molecular structure and the change referred to on p. 12 due to defects, enclosures or changes in uniformity of texture often reduce the strength more or less rapidly until the working load may exceed the ultimate strength and fracture occurs.

This tendency to weakening is more apparent when the metal contains certain impurities, *e.g.* sulphur in steel, or is in certain conditions due to treatment. It is, however, impossible to generalise. Tests for fatigue are carried out by subjecting a prepared test piece to alternating stresses, and counting the number of applications required to produce rupture.

Much ingenuity has been displayed in designing machines capable of producing alternation or reversals of stress. The number of applications is so large that it is necessary to produce them rapidly, to shorten the period, and to count them.

In Haigh's machine—a direct stress machine—the pull on the specimen is effected by an electro-magnet excited by a two-phase alternating current.

In Wohler's machine a short cylinder of the metal has a middle portion turned to a smaller diameter than the ends, one of which is firmly held in a revolving chuck at the end of a suitable bed over which the test piece projects. On the free end of the test piece a ball-bearing supporting a weighted scale pan is hung. This remains vertical as the piece revolves and provides the alternating stress which ultimately produces fracture. The revolutions are counted.

Millions of reversals may be required.

Practical bending tests in which the material is bent backward and forward through a definite angle till fracture occurs are sometimes used. The force employed exceeds the elastic limit of the material and is not of the nature of a fatigue test, although it may provide the user with much useful information on the toughness of the material. Col. Sankey's test is of this class.

In all tests other than direct tests there is always an attempt to establish a connection between the behaviour of the metal under that

particular method of examination and the results of a tensile or other direct test. These are in many cases extremely difficult and complicated. For this reason engineers adhere to the direct evidence afforded by a tensile test with bend or other tests as may be deemed desirable.

Plate and sheet metal required for cold stamping and pressing is subjected to standardised cupping tests. In Erichsen's machine, discs of the metal of a given size held at the edge are forced by a suitable tool with a round end through a cavity of given diameter to form a cup. The depth to which it can be forced without fracture expressed in millimetres is a measure of its "drawing" quality for metal spinning or "press die" work.

The "**modulus of elasticity**" is the force that would be required to double the length of a bar if its elasticity remained perfect. The "modulus" is an index of the stretching capacity of the metal.

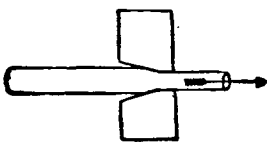


FIG. 21.

Ductility is the property which permits of the body being drawn out in the direction of its length—that is, converted into wire. The metal from which the finest wire is producible is the most ductile. Wires are produced by dragging rods of a convenient size through holes in a steel-faced plate.[1] The holes are somewhat smaller than the rod itself. By repeating the operation a sufficient number of times it is reduced to the desired gauge. The hole is slightly tapered and the end of the rod is ground thinner to permit of its being thrust through the hole far enough to allow it to be gripped tightly. A suitable lubricant is applied.

The property is dependent principally upon the tenacity and upon the ease with which the metal suffers deformation. Metals which have a low yield-point are moderately soft, and, if fairly tenacious, are most ductile. On this account gold and silver head the list of ductile metals, and iron precedes copper, tin, and lead, whose tenacity is much inferior, although they yield more readily than iron. Since the force applied must be concentrated on the section of smallest area—*i.e.* the area of the hole through which it is passing—it is obvious that tenacity will be the dominating factor. Any condition tending to lower the tenacity, increase the hardness, or raise the yield point will tend to diminish the ductility. Hence, pure metals of uniform structure are usually most ductile, and as the tenacity generally falls with increased temperature, all wires are drawn cold. If it were possible to maintain the tenacity while lowering the yield point they might be drawn hot.

In wire-drawing the metal becomes hard and brittle, and requires to be frequently annealed. Pickling in acid is also resorted to to remove films of oxide, when necessary.

[1] Fine wires and wires of accurate gauge are drawn through diamond dies Dies are also made of "widia" and other hard materials.

Some indication of the ductility of a metal is obtained from the amount of extension and reduction in area which takes place in carrying out a tensile test.

Wire-drawing in most cases increases the density, the force employed being converted into pressure by the conical form of the hole through which it is drawn.

ORDER OF DUCTILITY.

Gold	Aluminium	Zinc
Silver	Iron	Tin
Platinum	Copper	Lead

Gold wires as fine as the threads of a spider's web have been drawn by enclosing the gold in silver, and dissolving off the latter in nitric acid after drawing down.

Malleability.—Metals which can be beaten out or otherwise extended in all directions by pressure are said to be malleable. The degree of malleability is measured by the thinness of the leaves it is possible to produce. This is governed mainly by the relationship existing between the tenacity and the yield-point hardness of the metal. The force applied must be sufficient to deform the material, but in this case is not confined to a narrow section, as in wire-drawing, but distributed through the mass. When the force required to deform the material exceeds the tensile strength of the section to which it is applied rupture takes place, so that ultimately a limiting thickness is reached. The property is therefore less dependent on tenacity, and consequently a great change is observed in the order of malleability as compared with the ductility. Copper, tin, and lead, it will be observed, precede iron, whereas the reverse is the case in the table of ductility.

Malleability is greatly affected by the presence of impurities in the metal. In some cases a trace of a certain substance is sufficient to destroy it. This is usually due to the impurity producing an alteration in the internal structure, such as the separation of the impurity, or a eutectic containing it, from the metal during cooling. Traces of bismuth, arsenic, or antimony make even gold brittle. Bismuth in copper destroys its malleability. It forms envelopes, more or less completely surrounding the copper grains. The intervening material is brittle. Any treatment which lowers the yield point and softens the metal will tend to increase the malleability unless the tenacity is reduced at a greater rate. Thus, many metals are rolled, beaten, and otherwise worked hot, *e.g.* iron and copper. In some cases overheating causes the metal to lose its malleability and become "burnt." This is most noticeable in the case of metals not quite pure or only commercially pure. The purest iron can be worked at higher temperatures than either poorer iron or steel.

Commercial zinc affords a striking instance of the effect of heat in this respect. In the cold, the metal is brittle and crystalline. At a temperature of 120° C. to 150° C. it is malleable, and can be rolled

into thin sheets; at a somewhat higher temperature it becomes more brittle than when cold. Sheets of zinc rolled at the proper temperature retain a considerable degree of malleability, and can be bent and worked like other sheet metals with a little care.

During cold rolling, beating and other operations the metal is annealed as required to remove the work hardening which takes place.

ORDER OF MALLEABILITY.

Gold	Copper	Lead
Silver	Tin	Zinc
Aluminium	Platinum	Iron

Plates, sheets, foil, and leaf are terms applied to different thicknesses of metal. Plates, sheets, and foil are generally rolled. Leaf is beaten out by hammering. Gold leaf $\frac{1}{250000}$ of an inch in thickness, and so thin as to transmit light, is commonly produced by hammering. Palladium leaf $\frac{1}{2000000}$ of an inch thick is now produced for "silvering" purposes. At the Great Exhibition of 1862, sheets of Russian iron were shown $\frac{1}{700}$ of an inch thick. These, it would seem, had been produced by hammering the sheets in packets with charcoal powder between. Various tests are applied to determine malleability, such as bending, hammering, etc. Such articles as rivets and angle irons should be very malleable.

Resistance to Impact.—Metals which have passed satisfactory tensile and other mechanical tests sometimes fail in use although no fault is apparent in the design. Usually, the parts that fail have been subjected to shocks or repeated repetitions of stress. Various methods of testing resistance to shock have been devised. In most cases a test piece of suitable dimensions has a notch of definite size and shape cut in the side. The bar is held in a vice—forming part of the testing machine—at the level of the notch, and the force required to break it, when struck at a definite distance from the notch, is determined. The foot-pounds of energy required by bars of the same size afford a means of comparison.

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FIG. 22.—Izod Impact Testing Machine.

In the Izod test a square bar, 1 cm. in the side, is used. The notch is 2 mm. deep, the sides have an angle of 45°, and the bottom is a round groove of 0·25 mm. radius. The bar is struck by a pendulum hammer 2·2 cms. from the notch. The results may vary, but good steel gives from 40–50 foot-pounds.

Impact Testing Machine.—Fig. 22 shows a standard Izod

machine. The pendulum hammer is capable of developing energy equal to 120 ft. lbs. at the moment of striking. A hardened steel knife edge forms the point of contact with the test piece. When the hammer strikes a portion of the energy is absorbed in breaking the specimen. The remaining energy carries the hammer forward to a point dependent on the amount absorbed and a loose pointer is carried forward—as shown—and indicates the movement on the graduated circular scale, thus registering the residual force.

The accuracy of the notch and the setting of the test piece in the vice-holder greatly influence the result and must be carefully scrutinised.

Impact tests are now included in all or nearly all specifications for steel and many other metals.

The greatest use of impact tests is the detection of unsatisfactory microstructure which may result from errors in heat treatment or working.

Toughness is the resistance to fracture which is offered by a metal bending after the yield point has been passed to such treatment as bending and twisting. It is the reverse of brittleness.

Most malleable metals are tough, but not always in proportion to their malleability. It is determined by the number of times the metal can be bent to and fro before breaking, or the number of twists that can be put on a wire or rod of given length.

In some cases, as in testing steel rails, a heavy weight is allowed to drop from a given height upon the rail resting on supports.

Purity is not always associated with the extreme of toughness (see Copper refining and toughening, p. 215).

Brittleness.—Metals are brittle when they break at the yield point or readily after that point has been passed. This may be due to unsatisfactory structure which may be natural to the metal, as in the cases of antimony and bismuth, or to the interference in structure caused by the presence of impurities, changes occurring during solidification leading to separation and segregation, heat or mechanical treatment, or to fatigue. Phosphorus in iron renders the metal "short" in the cold—"cold short." Sulphur has a similar effect at a red heat—"red short." Cold-short iron works fairly well above a red heat, and red-short below that temperature. The term "short," as applied in this connection, means lack of toughness and malleability.

Flowing Power.—Metals which in the *solid* state can be readily shaped into any required form by pressure are said to possess the flowing property. Stampings, lead pipes and rods, coins, medals, etc., are made by taking advantage of this property. It does not in any way refer to the fluidity of the metal when molten, the operations being conducted upon the metal in the solid state.

The property seems to depend upon a combination of malleability, ductility, and toughness, allied to a peculiar structure giving the metal a semi-plastic character, which permits of the particles rolling over each other freely. When metals "flow," the movement of the particles

is generally throughout the mass. The effect of the pressure is identical with fluid pressure, and is uniformly transmitted, and the movement resembles that of a viscous liquid. The manner in which the metal moves is very important. To ensure strong reliable products the " flow lines " should be uniformly distributed and follow the distribution occurring in the original material.

Fig. 23 shows a satisfactory distribution, and Fig. 24 unsatisfactory distribution in a rivet.

Note.—Flow lines can be revealed by very carefully etching a polished section of the material.

Lead possesses the power of " flowing " to a great extent. In

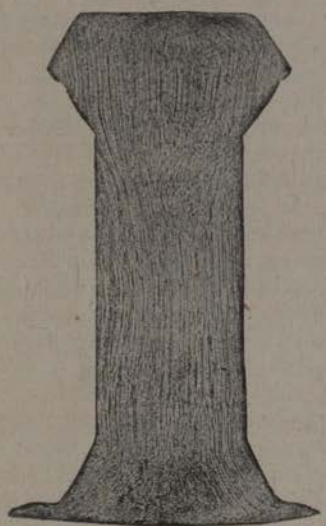


FIG. 23.

FIG. 24.

consequence of this, the plumber is able to work up by gentle hammering lead vessels from sheet, the superfluous metal being gradually worked away into the sides, making them thicker.

Lead pipe is squirted from a solid ingot by means of hydraulic pressure, the tube being formed by a mandrill or die, as it passes from the press. Delta metal is also extruded.

Many other applications of the flowing property are now being employed. Die-drawn and pressed work, sheet spinning operations, and the perforation of ingots prior to drawing into tubes may be mentioned as further examples.

In striking medals and coins, a disc of metal (a blank) is placed between steel dies, and the sudden application of pressure causes it to flow and fill all the finest lines of the die. The great sharpness of

medals and coins is due to this method of production. If cast, the metal would solidify before completely filling the mould owing to its thinness.

Welding.—The modern application of this term has led to some misunderstanding. Welding, strictly speaking, is the method of joining solid metals, reduced to a satisfactory condition, by simple pressure, whether by hammering or otherwise, no solder or fused metal being employed.

Methods where fused metal of the same nature as the pieces to be joined is used should be described as "burning" operations or autogenous soldering. Where the metal used is of a different character the operation should be included under "soldering" operations.

In welding it is essential that the surfaces in contact shall be perfectly clean and free from oxide, and the metal in a condition to "flow" readily under pressure. Gold fulfils both the conditions, and welds readily in the cold. Platinum is free from oxidation, but requires to be strongly heated to flow well under pressure. Most metals oxidise on exposure to air, especially when heated. The presence of an oxide film prevents welding. For this reason lead and tin are difficult to weld unless protected or so treated as to expose fresh surfaces during the operation, as in rolling or extrusion. Such fresh surfaces weld readily. In this way compound sheets of tin-faced lead foil are produced. Many other compound sheets are made in the same way, special care being taken to ensure that the plates of metal originally used are in the best possible contact, and so fitted as to exclude air in order that the fresh surfaces developed shall not be tarnished and the welding prevented. Copper, iron, and nickel, and other metals are welded in this way.

In the case of highly elastic metals, such as iron and steel, it is necessary to soften them and lower the yield-point by heating sufficiently to enable them to flow readily under the pressure or hammering employed. Oxidation takes place, and to obtain a good weld the oxide must be removed. In welding iron the metal is either made hot enough to fuse the oxide formed, or sand is used, which, by combining with the oxide, forms a fusible body (silicate of iron) which melts at a lower temperature than the magnetic oxide of iron which is formed on heating. This enables the removal of the oxide to be effected at a lower temperature and reduces the risk of burning the metal when a big weld is being made. In either case, when the pieces are placed together and the metal hammered the fluid matter is squeezed out (hammer slag), and chemically clean surfaces come into contact. The strength of a weld depends largely on the complete expulsion of the slag, and the surfaces are made more or less rounded to ensure this taking place. Borax is often used instead of sand, especially in welding steel. It produces a more fusible slag, and thus allows the welding to be done at a lower temperature.

The metals which weld readily are platinum, gold, silver, lead, tin, iron, and nickel.

In electric welding, the ends to be united are placed together, and a powerful electric current of low tension is passed by suitable connections from one piece across the point of contact to the other. The high resistance at the junction, owing to the poor contact, causes the development of intense local heat, which is greatest at the faces to be joined. When hot enough, the ends are forced together by a screw attachment, and union between the pieces takes place. (Thomson's Process.)

In welding large iron tubes made from plate, rings, etc. the electric arc is employed, the arc being sprung between the work itself, suitably supported, and carbon rods manipulated by hand or otherwise suspended above it. (Bernado's Process.)

Fusion Welding.—Metal burning, Acetylene welding, Metallic-arc welding, Quasi-arc welding, and other methods of a similar type belong to the same class of operations as lead burning, a very much older process.

Lead burning consists of uniting sheets or other articles of lead by melting the edges together in order to avoid the use of solder, a strip of lead being melted on the seam to ensure union. This is done in constructing sulphuric acid chambers and other chemical plant in order to avoid the electrolytic corrosive effects resulting from the presence of two metals. An oxy-gas or oxy-hydrogen blowpipe is used.

In acetylene welding a metal rod similar in character to the work, is melted into the joint, the suitably shaped *surfaces* of which are melted and unite with the metal from the rod. An oxy-acetylene blowpipe is used. Iron, aluminium, and other metals are thus welded.

In both cases the conditions of success are the same, viz. fusion of the surfaces to be joined, without overheating the bulk of the metal. It is, therefore, necessary to employ an intensely hot flame to enable the heating to take place almost instantaneously before the heat can be conducted into the body of the metal. In lead burning hesitation is fatal, and in acetylene welding, delay greatly increases the difficulties due to overheating and contraction. The latter consideration has always to be taken into account, and is dealt with in various ways.

In quasi-arc and other forms of electrode welding the principles are the same, but the heat is derived by using the rod of metal employed in making the joint as the conductor of an electric current. The joint is touched with the rod and a small arc sprung between it and the work, so that the heat developed by the arc heats the work and melts the rod which furnishes the added metal. When one rod is melted another is used. The electrodes employed are covered with a coating of fusible material. This melts and forms a slag which protects the molten metal, preventing oxidation and burning, and also chilling. The quasi-arc electrodes are covered with blue asbestos.

Soldering and Brazing.—In soldering, union is effected by employing a metal or alloy of lower melting-point, differing in character from the metal or metals to be joined. The metal or alloy employed

must alloy superficially with the surfaces of the metal to be united. To ensure this the surfaces must be mechanically and chemically clean, and suitable solders must be employed. Various fluxes are used to prevent oxidation and to remove oxides, if formed.

Tallow is used by the plumber, and resin, and zinc chloride, and sal ammoniac are largely used as fluxes for soft soldering where the temperature is low. In brazing and hard soldering borax is employed. See p. 44.

Soft soldering, brazing, silver and gold soldering are all forms of the same type of operation, different alloys and fluxes being used as occasion demands.

Conductivity.—Metals are, speaking generally, good conductors both for heat and electricity. Their relative conducting powers are as follows :—

	For heat.[1]	For electricity.[2]
Silver	1000	1000
Copper	748	941
Gold	548	730
Aluminium	—	511
Zinc	—	266
Platinum	94	166
Iron	101	155
Nickel	—	120
Tin	154	114
Lead	79	76
Bismuth	18	11

Electrical conductivity is greatly diminished by a rise in temperature and by impurities. Impure copper may have a conductivity little superior to that of iron. Alloys as a rule are poor conductors, but are less affected by heat.

[1] Matthieson. [2] Franz and Wieldemann.

CHAPTER II

METALLURGICAL TERMS AND PROCESSES

COMPARATIVELY few metals are found to any great extent in the metallic condition. When occurring in that form they are said to be **native.** The whole of the platinum, and practically all the gold used, are thus found. Iron, silver, copper, mercury, bismuth, and arsenic also occur native in notable quantities.

Native metals may occur in masses of considerable size, as threads and filiform masses penetrating the rocks, in grains and thin flakes, more or less minute, distributed through the rock mass or in alluvium, and associated with other substances containing the metal.

N.B.—Masses of native copper 500 tons weight have been found in the Lake Superior district, and nuggets of gold weighing 183 lbs. in Victoria. A nugget of silver weighing 4402 lbs.[1] has been found in Canada. Alluvium is the *débris*—sand and gravel—which results from the wearing down of rocks.

Metals generally occur in chemical combination with other elements, whereby their metallic character is completely masked. When a mineral contains a sufficient quantity of a metal combined with some element from which it can be readily separated, so as to render the extraction of metal of good quality profitable, it is said to be an **ore** of the metal.

The ores other than those containing the metal in a metallic state may be divided into three groups—

(1) Sulphurised and arsenical ores, those consisting of sulphides and arsenides, and including sulph-antimonides and tellurides.
(2) Oxidised ores, including oxides, hydrated oxides, carbonates, silicates, and phosphates.
(3) Haloid ores, including chlorides, oxy-chlorides, bromides, iodides, and fluorides.

A few mineral species, such as sulphates, might be included in either groups (1) or (2).

Sulphides, arsenides, and the other minerals included in group (1) are usually heavy minerals with a strongly marked metallic lustre. The colour varies from silvery white to coppery red, and usually they are brittle. Galena (lead sulphide), stibnite (antimony sulphide), copper pyrites (sulphide of copper and iron), and kupfernickel (nickel arsenide) may be taken as examples. Two notable exceptions are cinnabar (mercury sulphide) and zinc blende (zinc sulphide). The former is red, and the latter varies in colour from cream to black. Both are without metallic lustre.

[1] Keeley Mine, Ontario.

Oxidised ores are generally without metallic lustre and the density is very variable. Some, like tin stone—oxide of tin—are very heavy. sp. gr. 7·1. Others, like garnierite—silicate of magnesium and nickel —are very light, sp. gr. 2·2. The colour is very variable. The only exception of note is specular iron ore, a form of oxide of iron, which has a metallic lustre.

The ores in the haloid group have no common distinguishing features.

Ores of all classes may occur crystallised or in a crystalline, massive, or earthy condition. Sometimes, as in the case of kidney iron ore, a form of red hematite, imitative forms occur. The following list indicates the combinations from which the common metals are usually obtained :—

Sulphides	Copper, lead, zinc, antimony, nickel, silver molybdenum, mercury, bismuth, and cadmium.
Arsenides	Nickel, cobalt.
Tellurides	Gold, silver.
Oxides	Iron, copper, zinc, tin, manganese, chromium, antimony, aluminium, and tungsten.
Carbonates	Iron, copper, zinc, lead, and manganese.
Silicates	Copper, zinc, nickel.
Phosphates	Lead.
Chlorides	Silver, copper.
Fluoride	Aluminium.

The quantity of metal required to make the working profitable depends on the value of the metal extracted, and the form in which it occurs. A few pennyweights of gold per ton of ore, if in the free state, can be satisfactorily worked ; while an iron ore must contain a high percentage of the metal to be profitable.

Iron ores also afford a good instance of the effect of the combination in which the metal exists. Iron pyrites contains 46 per cent. of iron, but it is combined with sulphur, from which element it is difficult to completely separate it, and the iron made from the material, after burning off the sulphur, is of inferior quality owing to the tenacity with which that element is retained.[1]

Ores are sometimes found in deposits following the general lie of the rocks in which they occur. Such deposits are known as **beds.** When the occurrence is irregular, the ore being accumulated at certain points, the deposit is called a **pocket** or **bunch.** Many ores are found in what appear to have been fissures or cracks, which have been filled up with material altogether differing from the rocks in which they occur. These deposits are called **veins** or **lodes.** They do not follow the stratification of the rocks, but cut through them at a greater or less angle. Veins of quartz are often called *reefs.* The line along which they reach the surface is the *outcrop.*

Owing to the action of the air, moisture, etc., the upper part of a vein is often entirely altered, and sometimes has spread over the

[1] Pyrites cinders containing copper, after treatment by the Henderson process, p. 234, are briquetted and smelted for iron. The process for extracting the copper removes the last portions of the sulphur also.

It is now possible by calcining methods to remove the sulphur almost completely, thus rendering pyrites cinders available as a source of iron.

surface, forming a *cap*; or the alteration may extend deeper, even to the water-line.

Such alteration may have led to a complete change of the chemical character of the vein, sulphides giving rise to sulphates and oxides, carbonates to hydrated oxides, etc.[1]

The rock lying on either side of a vein is the *country* rock.

Veins are filled with various materials, some of which may be metallic ores and others not. Often lumps of country rock are also included. In Fig. 25 the black portions are the ore bodies. The material filling the vein is known as *veinstuff*. The non-metallic minerals commonly found as veinstuff are quartz, chlorite, felspar, mica, hornblende, and other silicates, barytes, fluor, calcite, dolomite, etc.

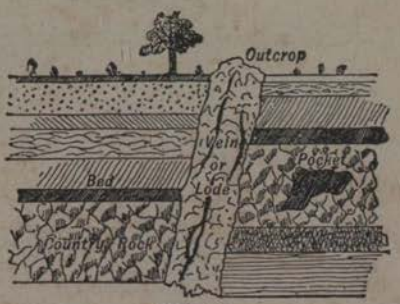


FIG. 25.

The operations necessary to separate these from the metallic portion are described as **ore dressing.**

Much of the ore often can be separated in a sufficient degree of purity by simply picking it over by hand, and breaking away adherent rock with a hammer. This is known as *hand-picking*.

When it is mixed up with the veinstuff more elaborate treatment is necessary. The methods employed take advantage of the specific properties of the materials comprised in the veinstuff, and are based on—

(1) Differences in specific gravity.
(2) Magnetic value.
(3) Electrostatic behaviour mainly dependent on conductivity.
(4) Flotation processes.

In each case it is necessary to break or crush the veinstuff in order to separate the metalliferous from the stony material. This is done by means of stone-breakers, crushing rolls, grinding mills, and stamps of various kinds, according to the fineness required. The metallic matter is usually denser than the non-metallic minerals with which it is associated.

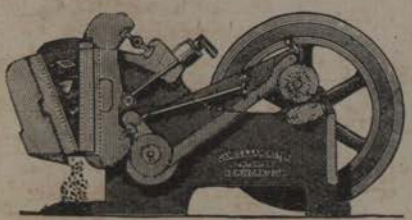


FIG. 26.—Stone-breaker.

Dry centrifugal separators are sometimes employed, but dressing operations utilising the differences in sp. gr. are generally carried out in suspension in water.

[1] See Iron.

Washing Operations.—Heavy substances settle out more rapidly when suspended in or agitated with water, and are less easily carried forward by a running stream than lighter ones, so that they are more easily deposited.

Material which is not too fine is washed in **jigs** (Fig. 27). These consist of sieves or shallow boxes with bottoms of wire cloth, suspended

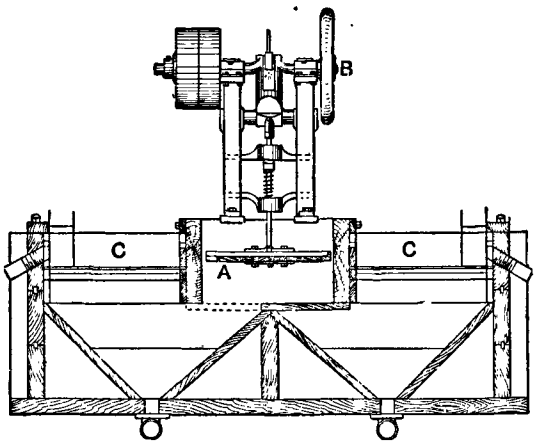


FIG. 27.—Plunger Jig. A, plunger; B, driving-gear for plungers; C, screens.

in water, and jerked up and down by mechanical means; or, the water is forced upward through the material in jerks by means of a plunger. The disturbance thus produced causes the heavy material to gravitate to the bottom, and the light matters can be scraped or washed off the top.

Finer material may be treated in hydraulic classifiers, in which the fine material meets with a current of water moving in the opposite direction —upward. The velocity of the water varies owing to the change in cross-section, and only the heavy matters are capable of gravitating to the bottom, from which they are removed. The lighter matters are washed away and matters of intermediate density remain in the classifier. It is essential that the particles shall be of uniform size. Fig. 28 shows a classifier of this type. Water enters at the apex, and the conical or pyramidal shape provides the means of producing a uniform reduction in the velocity. Special means are provided for the removal of the accumulated heavy matter.

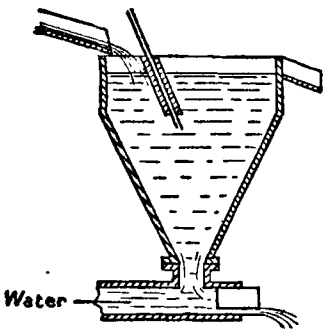


FIG. 28.

Other appliances for treating fine material depend on the flow of water down sloping surfaces, either in an uninterrupted manner or assisted by a jerking movement in the appliance.

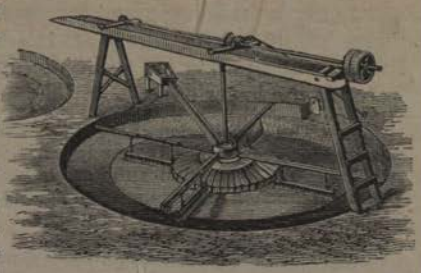


FIG. 29.—Buddle.

Buddles (Fig. 29) are circular, slightly conical tables, upon which the fine material, suspended in water, is fed at the apex. Water is supplied, and the ore stirred by brushes attached to revolving arms. The light portions are carried away by the water, and the heavy material accumulates on the cone, the heaviest nearest the apex.

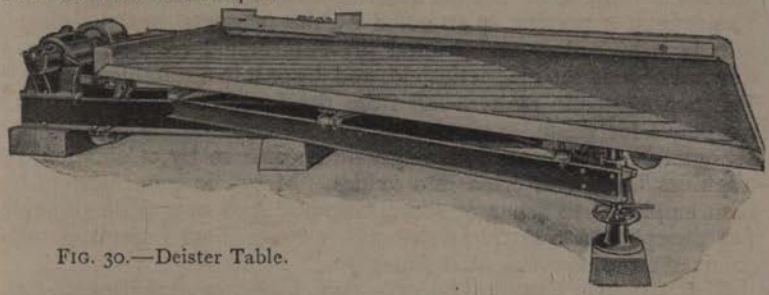


FIG. 30.—Deister Table.

Racks and Washing-tables are inclined tables on which the material is placed at the higher end and washed down by a gentle stream of water, being pushed back against the current by brushes or rakes. The light stuff is washed away.

The **Frue Vanner** (Fig. 31) and similar machines consist of a wide endless belt of india-rubber so stretched on rollers that the top forms an inclined table. A rapid shaking motion is communicated to the table, and the belt slowly travels in an upward direction. The fine stuff is fed with water from the trough at the higher end, and clean water is also sprayed on to the table. The current, aided by the jerking motion, separates and carries off the earthy matters, and the heavy metallic portions are carried on by the belt and washed off in the trough under the frame. Vanners are specially suitable for treating very fine material.

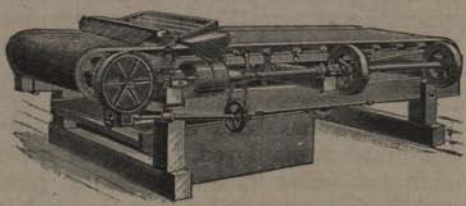


FIG. 31.—Frue Vanner.

Wilfley and other percussion tables consist of a slightly sloping rigid table with low undulations or ribs on the surface. This is

constantly jerked in a given direction so that the heaviest material in virtue of its inertia slowly travels upward to the higher corner of the table and passes off, while the lighter material passes off with the water at the lower edge.

Note.—The introduction of " Flotation " processes and the possibility of higher dressing concentration with less loss has led to an increasing tendency to finer crushing. This necessitates the use of more classifiers and tables with a corresponding reduction in the number of jigs and other similar appliances. Tables with rubber riffles and tops are now employed.

Magnetic Concentration.—Iron and other ores which are affected by magnetic influence can in some cases be separated by magnetic separators. The magnets—permanent or electrically excited—are protected by a thin moving screen of non-magnetic material such as brass or a leather belt. The crushed ore is brought into the field in some suitable manner, such as on a moving feed belt. The magnetic portion is attracted by the magnets, but the moving skin by which they are covered prevents actual contact, carries it forward beyond the magnetic field, and drops it in a suitable receptacle. The non-magnetic matters fall from the feed-belt unaffected into a receptacle for waste.

Some ores which are not magnetic become so by calcination, the sulphides being converted into oxides. Magnetic concentration has been employed to separate some magnetic iron ores from sulphides and phosphates to enable rich ore free from those impurities to be obtained from contaminated deposits.

Electrostatic Concentration.—Some progress has been made in adapting electrostatic attraction to secure separation. The attractions and repulsions to and from an electrically charged surface depend on the ease with which induction and discharge can take place. Obviously the better conductors will be most readily affected, and by suitably regulating the movements of inclined surfaces the metallic material may be separated from the non-metallic.

Flotation Processes.—These have become very important, for intimately mixed finely-divided minerals. If finely-divided materials in a state of admixture be introduced into water to which small quantities of a suitable oil or other material have been added, and the water agitated violently with air, a froth is formed which includes the particles of any solid bodies affected by the oil or other additions made. Formerly additions of acid were commonly made, but the acid circuit has been discontinued and alkali (carbonate of soda) is now often employed. There is great variety in the methods of treatment followed, but, speaking generally, the minerals with a metallic lustre are included in the froth, and can be removed with it. The stony matter is not floated. Rapidly revolving paddles and air jets are employed to produce agitation, and the oil and ore feed are steadily maintained in proper proportions. This method of treatment enables finely divided material in small quantities to be removed from stony matter. Brittle ores, like copper pyrite, which is very

difficult to dress on account of the losses due to fines, can be treated and intimate mixtures of galena and zinc blende—blue ore—can be separated.

In flotation processes the addition of suitable reagents may ensure the " flotation " and removal in the froth of one mineral and the " depression " of another so that it is removed in the tailings.

Zinc and lead sulphides may be thus separated.

Pine and other oils, Cresylic acid and Xanthates are employed.

The heavy material is floated upward with the froth, hence the name. The oil and other substances added affect the surface tension

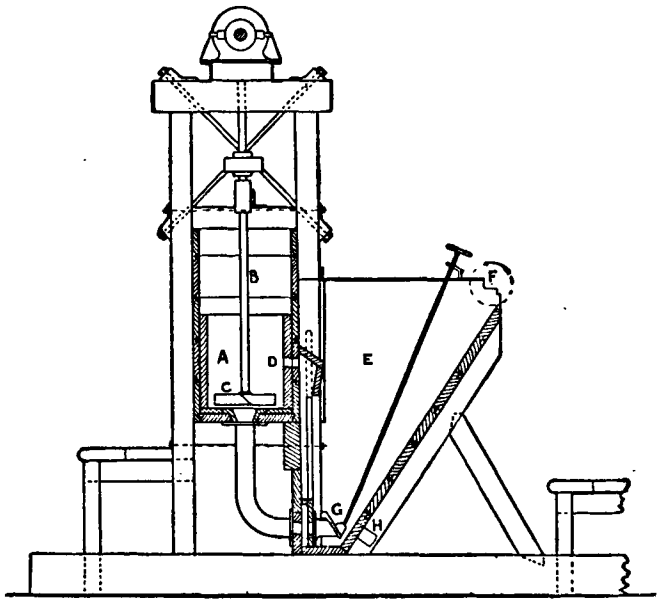


FIG. 32.—Froth flotation unit. A, cell; B, revolving shaft; C, paddle; D, outlet E, separating chamber; F, froth remover.

of the water, and determine whether or not any particular mineral is taken into the froth. Figs. 32 and 33 show a froth flotation unit and plant.

The dressed ore as delivered by the miner to the smelter is still impure. The earthy matters associated with it are known as **gangue.**

Smelting.—The ore as received from the mine may not be in a satisfactory condition to admit of the direct extraction of the metal. The form in which the metal occurs may not be that from which it is most easily or perfectly separated, or the mechanical treatment by dressing may not have been capable of removing the associated matters to a sufficient extent. Thus some metals occurring as sulphides are most easily obtained from the oxide, *e.g.* zinc. In other cases, *e.g.*

copper and nickel, the amount of the metal in the ore is often small and is associated with iron pyrite, from which the dressing operations cannot separate it. In all such cases the actual extraction of the metal is preceded by operations to obtain the best combination or to concentrate the ores by methods which produce a rich intermediate product.

The various operations whereby the metal is separated *by fusion* from the ore are known as *smelting*. The smelting campaign often involves several distinct operations.

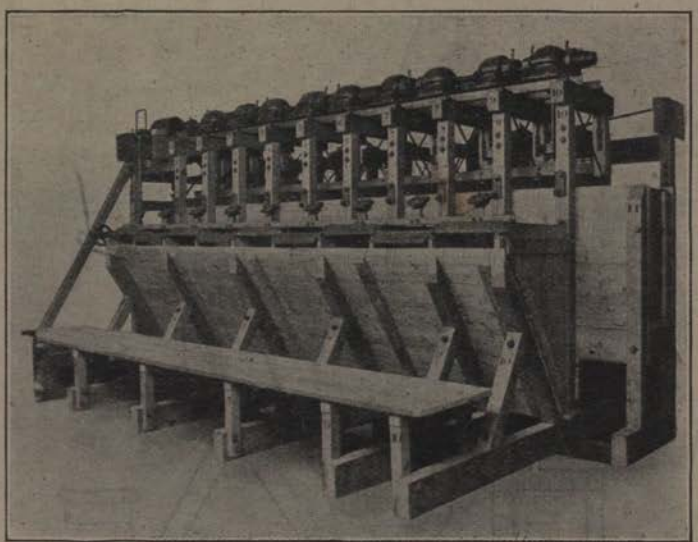


FIG. 33.—Froth Flotation Plant. Minerals Separation Co.

The preliminary treatment to which the ores are subjected generally takes the form of heating them in a plentiful supply of air. This process is called **calcination.** By this means the sulphur in sulphides is burnt off as sulphur dioxide, which being gaseous passes away, and the metal at the same time also takes up oxygen from the air, and is converted into an oxide, or, the removal of the sulphur may only be partial, and a sulphate may result—

$$\underset{\text{Lead sulphide}}{PbS} + \underset{\text{Oxygen from air}}{3O} = \underset{\text{Lead oxide}}{PbO} + \underset{\text{Sulphur dioxide}}{SO_2}$$

or $$2PbS + 7O = PbO + \underset{\text{Lead sulphate}}{PbSO_4} + SO_2$$

The sulphides of iron, copper, zinc, and lead thus form sulphates during calcination. The amount formed depends on the temperature and other conditions

of the roasting. With the exception of lead sulphate, they are decomposed by strongly heating them. Iron, copper, and zinc sulphates yield oxides. Silver sulphate is reduced to metal.

Arsenic is similarly removed as white arsenic, As_4O_6 (see Tin Smelting), and antimony to some extent as antimonious oxide, Sb_2O_3. During calcination other changes of great importance take place. Carbonates are decomposed with the expulsion of carbonic acid gas (CO_2), leaving an oxide of the metal.

$$\underset{\text{Zinc carbonate (Calamine)}}{ZnCO_3} = \underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Carbonic acid gas}}{CO_2}$$

Moisture is expelled, and in some cases oxides containing the lower proportion of oxygen are converted into higher oxides. This is sometimes of great importance, as in iron smelting. The introduction of ferrous oxide (FeO) into the furnace would seriously impair its working, besides causing loss of iron in the slag. All ores, therefore, containing this oxide must be calcined before introduction to the furnace, when the following change occurs :—

$$\underset{\text{Ferrous carbonate}}{3FeCO_3} + O = \underset{\text{Magnetic oxide of iron}}{Fe_3O_4} + 3CO_2$$

or $$3FeCO_3 = Fe_3O_4 + 2CO_2 + CO$$

Calcination also leaves the material in a more open and porous state, and it is thus more readily acted upon during reduction. especially by gaseous reducing agents such as carbon monoxide.

The term "roasting" is often used in the same sense as "calcining." In copper smelting it only applies to the operation in which the metallic copper is separated.

Most metals are converted into oxides by calcining. Gold, platinum, and other precious metals and silver are not affected.

Reduction.—The separation of the metal from chemical combination is known as *reduction*. If an oxide, this is generally done by heating it with carbon or carbonaceous matters, such as charcoal, coal, or coke ; the carbon of these substances combining with the oxygen and forming CO_2 (carbonic acid gas) or CO (carbon monoxide) according to the temperature at which the reduction occurs. Carbon monoxide itself is a powerful reducing agent, combining with oxygen and forming CO_2. Hydrogen reduces oxides with the formation of water (H_2O). Hydrocarbons act in a similar way.

Goldschmidt (Thermit) Process.—The oxides of many refractory metals, such as chromium,[1] molybdenum, manganese, as also iron, are reduced by this process. Aluminium is employed as the

[1] Chromium as an addition to steel is now being reduced by silicon and ferro silicon directly in the steel furnace, a mixture of chrome ore and the reducing agent being added to the bath.

reducing agent. The powdered oxide of the metal is mixed with finely granulated aluminium and the mixture ignited in a suitable manner. A priming powder of barium peroxide and very fine aluminium or magnesium may be employed, the ignition being effected by a strip of magnesium ribbon, one end of which is embedded in a small portion of the priming powder. The free end of the ribbon is ignited, and the combustion rapidly extends through the mass. The aluminium forms alumina (oxide of aluminium), and the temperature rises so high that the alumina—M.P. 2050° C.—fuses. Substances employed to liberate the metal from chemical combination are known as **reducing agents.**

Sulphides are sometimes reduced directly to the metallic state by heating with iron or with iron-bearing materials. Thus galena (sulphide of lead) yields sulphide of iron and metallic lead :

$$2PbS + 2Fe = 2FeS + 2Pb$$

and stibnite (sulphide of antimony) yields sulphide of iron and antimony—

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb$$

In this case the iron unites with the sulphur, and liberates the metal.

Sulphides are often reduced by **air-reduction processes.** Thus cinnabar (sulphide of mercury) is reduced by simple heating in a current of air. The sulphur burns off, leaving the mercury—which is volatilised by the heat—free. The vapour is condensed.

$$HgS + O_2 = SO_2 + Hg$$

Silver sulphide is similarly reduced.

The mutual reactions of oxides, sulphides, and sulphates are sometimes employed to liberate the metal. All the sulphur and oxygen in the compounds pass off as sulphur dioxide. See copper and lead, pp. 215, 241.

Sulphides are also reduced by calcining to oxides with the subsequent reduction of the oxide by carbonaceous or other reducing agent, *e.g.* zinc occurs as sulphide, but is best obtained from the oxide—

$$\underset{\text{Zinc sulphide}}{ZnS} + 3O = \underset{\text{Zinc oxide}}{ZnO} + \underset{\text{Sulphur dioxide}}{SO_2}$$

(Oxygen)

$$ZnO + C = \underset{\text{Carbon monoxide}}{CO} + Zn$$

Smelting operations are conducted at a temperature above the melting-point of the metal. Most metals, after reduction, are obtained in a fused state, and, being heavier than the other materials, run down and form a lowermost layer in the furnace or crucible.

Volatile Metals.—Zinc, mercury, cadmium, sodium, and potassium are vaporised at the temperature of reduction, and the vapours are led away and condensed.

Fluxes.—The infusible earthy matters often present in ores may seriously impede the collection of the reduced metal, or retard the reduction by enveloping it and preventing the action of reducing agents, or, by combining with it chemically at the high temperature, cause loss of metal in the slag. It is therefore necessary in smelting to provide means for causing them to be liquefied at the furnace temperature. This is done by mixing with the ore and reducing agent some substance which either melts itself and dissolves the infusible matter, or, by combining with it in the furnace, forms a substance which is fusible at the temperature employed.

Fluor spar, for example, dissolves barytes and phosphate of lime, and lime combines with clay and forms a fusible body.

Substances added to the furnace charge for this purpose are called *fluxes*.[1]

Most fluxes act to a large extent both chemically and physically. The earthy matters to be removed are divisible into two great classes. Those consisting of earthy metallic oxides and carbonates (the CO_2 is expelled during smelting, and oxides are produced), such as limestone, dolomite, etc., are *basic* in character ; silica (quartz, sand, etc.), and many other substances containing it, are known as *acid* gangue. When silica is heated with metallic oxides, combination takes place, and bodies called silicates are produced. Thus, lime and silica form silicate of lime, and so on. Some of these melt readily, others only at the highest temperatures. The fusibility depends on the nature of the metallic oxide, and on the amount present. Silicates of soda and potash, lead, manganous and ferrous silicates melt comparatively easily, but silicates of lime, magnesia, alumina, and zinc are practically infusible at ordinary furnace temperatures. As in ordinary cases of solution, where the presence of a soluble body depresses the freezing-point and lowers the melting-point, so the presence of mutually soluble silicates lowers the melting-point of the mixture. In this way silicates with high melting-points may be rendered fluid at much lower temperatures by the presence of another. When, therefore, more than one metallic oxide (base) is present in combination with the silica, forming a compound or complex silicate, the mixture of the two silicates is more readily fusible ; the more fusible the silicates employed are separately, the lower will be the temperature at which the mixture will melt. Thus, common soft glass is a mixture of silicate of soda and silicate of lime ; flint glass, of silicates of lead and potash. Thus also, by mixing silicates of lime and alumina or magnesia, fusible bodies are produced.

From the foregoing it will be seen that the selection of a flux will depend on the nature of the gangue to be removed. If *silica* only, then some oxide whose silicate is fusible, as oxide of iron, must be employed, or two bodies such as lime and alumina or magnesia. If clay (silicate of alumina) is to be removed, an addition of lime is all that is necessary, the other base, alumina, being already present.

[1] *Fluo*, to flow.

If *metallic oxides, or basic bodies*, have to be fluxed, silica must be added, and, if necessary, a second metallic oxide, *e.g.* oxide of iron, to produce a fusible body.

The substance produced by the combination of the flux with the gangue is called a **slag** or **cinder.** In most cases slags are mixtures of silicates, and thus partake of the chemical nature of glass. Their appearance depends very much on the rate of cooling, and their composition. Rapid cooling gives a glassy, and slow cooling a stony appearance. When gases escape during solidification, the slag is full of holes—vesicular or spongy.

The principal materials employed as fluxes are—

Substance.	Character.	Composition.
Lime	Basic.	CaO
Limestone	,,	$CaCO_3$
Mountain limestone	,,	$CaCO_3MgCO_3$
Alumina	,,	Al_2O_3
Clay	Acid	Al_2O_3 and SiO_2, etc.
Quartz, sand, etc.	,,	SiO_2
Oxide of iron and slags containing it	Basic	Fe_2O_3 and Fe_3O_4 [1]
Fluor spar	——	CaF_2

Garnet, felspar, and other natural silicates are sometimes employed. **Borax,** and carbonate and sulphate of soda are also used in small quantities in special operations. Borax is sodium biborate, and dissolves metallic oxides, forming fusible borates. At high temperatures, the soda it contains combines with silica, and thus acts as a flux for that substance. The use of fluor as a flux for barytes and phosphate of lime (bone ash) has already been referred to. Fluor is also a flux for silica. When strongly heated together, a *gaseous* fluoride of silicon is formed and lime remains, which is fluxed in the usual manner.

$$2CaF_2 + SiO_2 = SiF_4 + 2CaO$$

The *bases* generally found in slags are lime, magnesia, alumina, ferrous oxide (FeO), manganous oxide, and smaller quantities of potash and soda.

Note.—The ferric and magnetic oxides of iron do not readily combine with silica, but when heated with reducing agents, ferrous oxide is formed, which is a powerful flux.

In many refining processes, slags are produced containing the metal under treatment. These are subsequently worked up for the recovery of the metal.

Most silicates are capable, when fused, of carrying in suspension or solution excess either of the metallic oxide present or of silica. The actual composition of the slag is dependent on the temperature. If excess of either component—acid or base—is available the slag will reach the limit of saturation. If the metallic oxide is in excess, the slag is said to be *basic*; if silica, it is described as *acid* or *siliceous.* Silicates are generally classified according to the ratio existing between the oxygen in combination with the metal and silicon respectively.

Sub-silicates	$4RO.SiO_2$	$4R_2O_3.3SiO_2$	2 : 1
Mono- ,,	$2RO.SiO_2$	$2R_2O_3.3SiO_2$	1 : 1
Sesqui- ,,	$4RO.3SiO_2$	$4R_2O_3.9SiO_2$	1 : 1½
Bi- ,,	$RO.SiO_2$	$R_2O_3.3SiO_2$	1 : 2
Tri- ,,	$2RO.3SiO_2$	$2R_2O_3.9SiO_2$	1 : 3

[1] After reduction to FeO.

A slag is *clean* when the metal has been so completely extracted as to permit of its being thrown away. An ore is said to be *self-fluxing* or *self-going* when the earthy constituents are fusible without the employment of a flux. When a mass of materials is fused, the substances formed separate according to their relative specific gravities, and the slag, being lightest, floats on the top. Sometimes metal, speiss, regulus, and slag are produced in the same operation. They arrange themselves in the order stated.

Concentration Processes.—The metallic contents of ores which are too poor to be directly reduced are sometimes subjected to a series of operations for the purpose of concentrating the metal in smaller bulk, from which enriched portion it is finally obtained. This is done by taking advantage of some chemical property manifested by the metal being worked for, to separate it from foreign matters.

Note.—The greater part of the copper obtained is produced from copper pyrites, $Cu_2S.Fe_2S_3$—a compound of iron and copper sulphides—which should contain 34 per cent. of copper. It is usually mixed, however, with so large a proportion of iron pyrites, FeS_2, that it seldom contains more than 12 per cent. of copper, and often less. The concentration of the copper is brought about by taking advantage of the superior affinity of copper for sulphur and of iron for oxygen. By calcining the ore, some iron and copper sulphides are changed to oxides, but on heating the whole to fusion, the copper oxide is decomposed by the unaltered iron sulphide remaining, copper sulphide and iron oxide resulting. The iron oxide is removed by fluxing with silica to the slag. The copper sulphide, being heavier, sinks to the bottom of the furnace. The material is thus enriched in copper, and after one or two treatments consists of practically pure sulphide of copper, from which the metal is extracted.

$$Cu_2O + FeS + SiO_2 = Cu_2S + FeO.SiO_2$$

Nickel is concentrated in a similar manner from poor ores.

A mixture of sulphides artificially obtained in this manner by fusion is called a **regulus**, or **matte**. Cobalt and nickel are sometimes concentrated as arsenides. The mixture of arsenides is called a **speiss.**

Refining Processes.—Metals when first obtained are never pure. The impurities consist of (1) small quantities of other metals simultaneously reduced; (2) non-metallic substances reduced in the furnace, *e.g.* silicon and phosphorus; (3) substances not completely removed by reduction, oxygen, sulphur; (4) substances taken up in the furnace, *e.g.* carbon and sulphur in iron, iron in antimony. The refining process adopted depends on the metal under treatment and the impurities to be removed. In some cases, as with iron and antimony, the reducing agents employed, carbon and iron respectively, are taken up by the metal to a certain extent. They are eliminated by heating the metal first obtained with more of the ore, oxide of iron in the case of iron (puddling), and sulphide of antimony with antimony. In each case further reduction takes place at the expense of the foreign matters present.

In most cases, however, the impurity consists of foreign metals present in the ore, and simultaneously reduced, together with sulphur, arsenic, and other non-metallic bodies.

Refining processes may be grouped as follows :—Processes depending on—

Liquation,
Oxidation,
Electrolysis.

Liquation includes all processes depending on differences in fusibility.

In some cases it is possible to separate the greater part of the impurity by carefully melting out the metal from the less fusible impurity. This is only possible when the impurity has separated more or less completely from the metal during solidification and does not redissolve at the melting-point of the metal.

In refining tin the impure metal is placed on the sloping bed of a furnace and gently heated. The tin melts and drains away, leaving the iron, arsenic, and copper with some tin as a pasty residue on the hearth. This is known as " hard head."

Zinc is separated from lead by maintaining the metal just above its melting-point. The lead, which is not soluble at this low temperature, gradually settles to the bottom. The lighter purified zinc is ladled off into moulds.

Sometimes the practice is reversed (see " Tin boiling," p. 309). The Pattinson and Parkes processes for the desilverisation of lead belong to the same category (pp. 250, 253).

Note.—The term is applied generally to the separation of matters according to their different melting-points, spontaneously, as during solidification or otherwise. Alloys are frequently not homogeneous from this cause.

In **oxidation processes** the metal is exposed at a high temperature or in a molten state, to the oxidising influence of the air in a suitable furnace. Impurities which have a greater affinity for oxygen, oxidise more readily than the metal in which they occur. In some cases the solubility of the oxide of the metal in the metal itself assists the removal, as the oxide carries the oxygen to the interior of the metal, and effects the oxidation of more oxidisable bodies. This is notably the case with copper, see p. 215. In the Bessemer process air is blown through iron. In other cases, as in the purification of iron by puddling, and in steel manufacture, solid oxide of iron is added to carry on the oxidation, thus reducing oxidation losses. The oxides which form are removed from the surface by skimming, or, if the heat is sufficient, unite with silica, and form fusible silicates. The method of conducting the operation, and the name it receives, differ with the metal under treatment.

Lead is thus *improved*, iron *refined*, copper *scorified*.

The term **scorification** (L., *scoriæ* = ashes) is also applied to a process in the dry assay of gold, silver, and other ores. A quantity of the silver ore is mixed with finely granulated metallic lead, placed in a clay dish (scorifier), and heated in a muffle until *about half the lead is oxidised*. The silver and gold are set free, and alloy with the residual lead.

Silver is purified by alloying it with lead and then removing the lead by oxidation. This is conducted on a *cupel* made of suitable porous material (see Silver), and the process is known as **cupellation.** The oxide of lead (litharge) formed is fusible, and is either run off the surface or partially absorbed by the porous bed. The silver and gold being unoxidisable are unaffected, and remain on the cupel. Base metals present are attacked by the oxide of lead, and the oxides formed, although not fusible at the temperature at which the process is carried on, are dissolved by the molten litharge and carried off, leaving the precious metals pure.

The separation of silver and other metals from gold is the object of the operation known as **parting.** This process consists of dissolving out the silver by the action of acid, leaving the gold unattacked.

Electrolytic extraction processes are employed for copper, zinc, and aluminium: see pp. 230, 235, 324, 332.

Electrolytic refining.—The impure metal is made the anode—dissolving pole—of an electrolytic cell. The cathode—depositing pole—consists of a pure thin plate of the metal under treatment, or one from which the deposit can be stripped. The impurities either remain in solution or are not dissolved. In the latter case they form a muddy deposit in the bath.

CHAPTER III

FURNACE TYPES

MOST metallurgical operations are conducted in structures specially designed either for the production and employment of high temperatures, or to secure perfect control of the temperature and gaseous atmosphere in which the process is carried on. In many cases, special features are introduced with a view to saving fuel.

Classification

(1) *Kilns and Stalls.*—Structures or enclosures in which the materials are mixed with the fuel, free access of air is permitted, and no fusion takes place.

(2) *Hearths.*—Shallow and more or less open fireplaces, in which the materials and fuel are mixed, a blast of air supplied, and the atmosphere made more or less oxidising by varying the amount of air supplied.

(3) *Wind Furnaces.*—Deep fireplaces, with grates at bottom and flue openings at top, for heating crucibles, etc. (p. 187). Many of these are now oil-fired.

(4) *Blast Furnaces.*—Tall structures in which the materials and fuel are mixed together, an air-blast introduced near the bottom, and in which fusion of the contents is effected.

(5) *Reverberatory Furnaces.*—Furnaces in which the fuel is burnt in a separate part of the structure, the flame and hot gases only coming into contact with the material treated.

(6) *Muffle Furnaces.*—Chambers which are heated externally by the flame and fire gases circulating in flues which surround them.

(7) *Tube and Retort Furnaces.*—Furnaces in which the operation is conducted in special vessels fixed in a chamber and heated externally.

(8) *Regenerative Furnaces.*—Those in which the waste heat is employed for heating the air, or air and gas, supplied to the furnaces.

Kilns.—Calcining operations are frequently conducted in vertical chambers provided at the bottom with a grate or with openings to admit air. The substance to be calcined is mixed with sufficient fuel, the burning of which generates the heat necessary to carry on the operation. Gjer's calciner for calcining iron ore is shown on p. 117.

Kilns are sometimes heated by gas or by the waste heat from furnaces.

Reguli and mattes are often calcined in stalls (Fig. 34) usually built in blocks, back to back. The back wall contains the main flue which communicates by the openings O, and by flues in the side wall

with the interior of the stall. The front is loosely built up, and the top covered with small stuff and a sheet of corrugated iron while the operation is going on. With reguli rich in sulphur, a good layer of wood at the bottom, to start the operation, is all the fuel required, the heat generated by the burning sulphur, etc., being sufficient to carry it on. Several calcinations are needed to completely remove the sulphur, a larger proportion of fuel being required each time. Coke or coal is frequently used in the later stages.

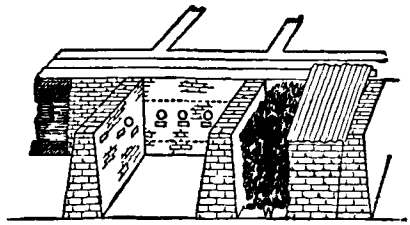


FIG. 34.

Fig 35 shows a simple **blast furnace.**[1] On examining the figure it will be noticed that the vertical furnace chamber has no grate, the bottom of the furnace being masonry or other solid material. An air-blast is supplied to the furnace by means of bellows, fans, blowers, or blowing-engines, through nozzles, which enter at D. These nozzles are called *tuyères*. The materials to be treated are charged into the furnace along with the fuel, and remain in contact with it throughout. As the substances melt, they run down to the bottom and accumulate in the space below the tuyères, known as the crucible, or hearth. When sufficient has collected, an opening—tapping hole—(kept stopped with clay) is made into the furnace, and the melted matters allowed to flow out, or they may flow out continuously into a separate receiver. It is obvious that in such furnaces fusions and processes of a reducing character only can be conducted, since the materials are heated in contact with carbonaceous bodies employed as fuel.

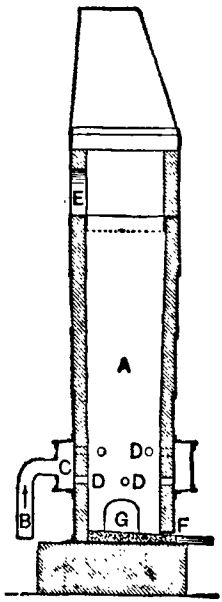


FIG. 35.—Foundry Cupola for melting Iron. A, stack; B, blast-pipe; C, blast-box; D, tuyères; E, charging opening; F, tap-hole; G, cleaning door.

Economy of Fuel in Kilns and Blast Furnaces.—In calcining in kilns, the air admitted at the bottom finds its way up through the descending hot material, and cools it, thus carrying the heat back into the kiln, while the descending column of cold material charged in at the top deprives the ascending current of hot gases (products of combustion, etc.) of much of its sensible heat, carrying it thus downwards into the kiln. For maximum economy of fuel, the combustion should take place in the middle region.

[1] See also Fig. 65, p. 122.

In *blast furnaces*, the combustion takes place near the region at which air is blown in, and the ascending stream of gases is cooled by the material in the upper part of the furnace, the degree of cooling depending on the rate of ascent and the height of the column. From the blast furnaces used in smelting iron, they escape at a temperature of from 200° C. to 500° C. As the temperature of combustion is high and the carbonaceous matter in excess, the carbon burns to carbon monoxide. Any attempt to burn this by blowing in air higher up the furnace is met with the difficulty of establishing a second region of combustion.

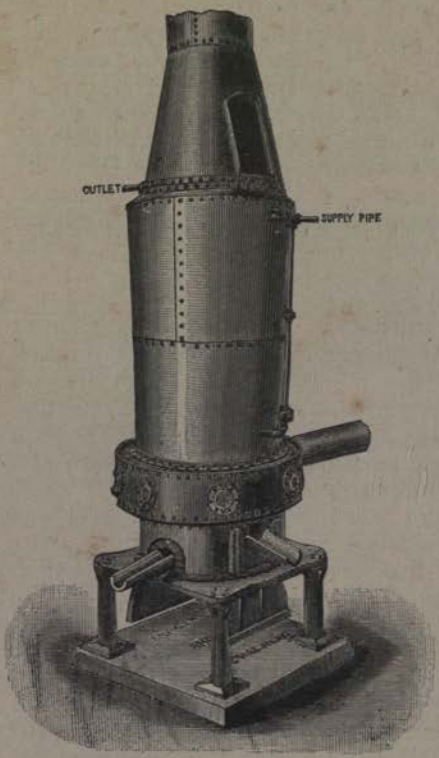


FIG. 36.

Fig. 36 shows what is known as a **water-jacketed furnace.** In these furnaces those parts subjected to the most intense heat and the action of corrosive slags, etc., are made of hollow iron casings through which water circulates, the cooling action of which prevents the iron from being affected.

Fig. 37 represents a type known as the **reverberatory furnace.** It will be seen that the chamber in this case is horizontal, and is divided into two unequal parts by a low partition (fire-bridge) crossing it. The smaller part is the *fireplace*, closed with fire-bars below, and having an opening for charging the fuel. The larger portion is the *laboratory*

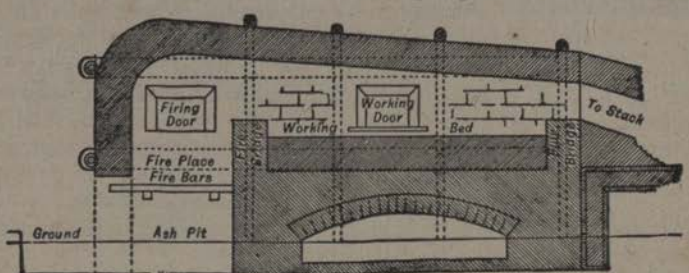


FIG. 37.

of the furnace, the bottom of which is the *bed* or *hearth*, and on this the materials are treated. Flues at the end opposite to the fireplace communicate with the stack or chimney. The roof gradually inclines towards the flues, and deflects (reverberates) the flame and hot gases from the fire downward, and, getting heated, radiates heat on to the bed. In furnaces of this class, it will be observed, the materials and fuel do not come into contact, and hence all kinds of operations can be conducted in them. Thus, by mixing reducing agents with the charge, reduction can be effected (see Tin and Lead Smelting), and by admitting air to the furnace-chamber, through openings in or near the fire-bridge, the substances under treatment are heated in contact with air, and oxidation (calcination)

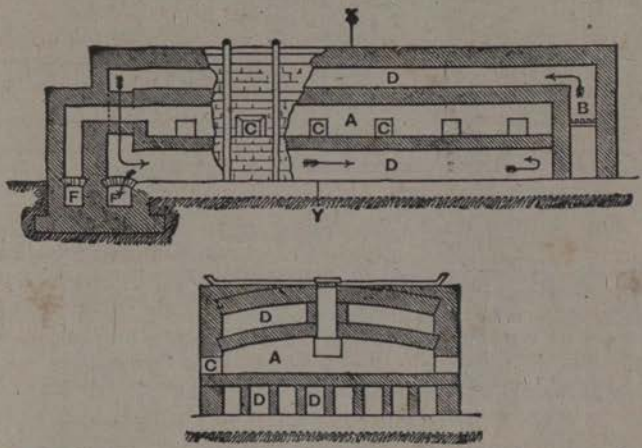


FIG. 38.—Muffle Furnace. A, chamber; B, fireplace; C, doors; D, flues round chamber; F, flues to stack and condensing tower.

goes on. Sometimes air is blown in, as in cupellation. By regulating the air-supply to the fire with dampers, the atmosphere can be made reducing or oxidising as may be required.

The draught is sometimes aided by forcing air through the fire by a steam-jet injector.[1] The steam issuing at high pressure from the nozzle at the mouth of the trumpet-shaped tube, entangles and carries forward the air. Not much steam is required, only about 5 per cent., at a pressure of 60 lbs. The horizontal branch passes under the fire-bars, and the ash-pit is closed by doors luted round with clay.

Muffle Furnaces.—In some cases it is necessary, for various reasons, to exclude the products of combustion as well as the fuel. In such circumstances *muffle furnaces* are employed. The muffle is a chamber surrounded by the fire, or by flues through which the products of combustion and hot gases from the fire pass. Such a furnace as used in copper extraction is shown in Fig. 38. Muffle furnaces are also used in annealing and heat-treatment processes, and in silver and gold assaying.

[1] See Fig. 55.

In **Regenerative Furnaces,** the heat carried away to the flues by the escaping gases is employed to heat the air supplied to the fire, and thus returned to the furnace, effecting a considerable saving in fuel. In gas-fired furnaces the gas is also heated before burning. Siemens's regenerative furnace is described on p. 195.

Tube and Retort Furnaces consist merely of a fire chamber in which retorts or tubes for the reception of the materials to be treated are suitably supported. They are employed in the extraction of bismuth, zinc, etc. (see p. 318).

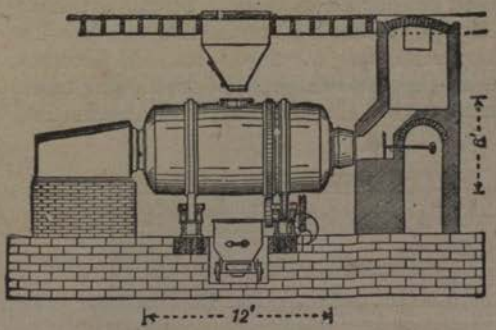


FIG. 39.—Brückner Calciner.

Mechanical furnaces of various forms, designed to effect mechanically what in ordinary furnaces is done by hand, are extensively employed. In calcining fine materials, the continual or repeated turning over of the material so as to expose it to the air, is necessary, and involves much manual labour. In the *Brückner* furnace (Fig. 39), this is done by putting the material into a brick-lined chamber, as shown, which can be caused to revolve slowly. The chamber is carried on rollers, and the motion communicated by the gearing shown. It makes about six revolutions per minute. The fireplace is stationary, and the flue is provided with a damper. In the White-Howell furnace (Fig. 40), the revolving chamber is placed at a small angle; the ore, fed continuously from a

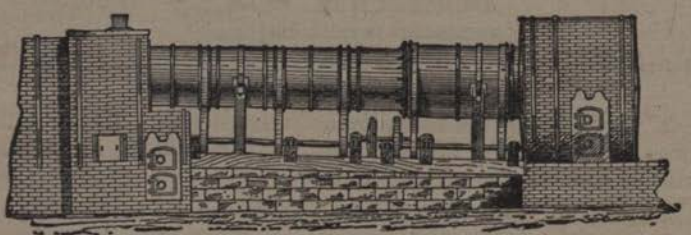


FIG. 40.—White-Howell Furnace.

hopper at the higher end, is gradually moved forward by the rotation of the chamber, being picked up by projections inside, and dropped again as the furnace revolves. The roasted matter is discharged at the lower end.

In tower furnaces, shown in Fig. 41, the fine material is allowed to fall down tall heated chambers, and meets in its descent an ascending current of hot gases from the fires F, and air admitted through suitable openings. The sulphur and other combustible bodies are oxidised, and the gases escape by the flue B. The door at C is for the removal of the roasted material, and DD to remove the dust carried over by the current of gases.

In Gerstenhoffer's calciner, the finely divided ore is fed on to triangular shelves crossing the furnace, and arranged so that each row of shelves catches what trickles from those above, and thus expose it fully to the hot air and gases from the fire.

In other forms of calciner, rakes and ploughs are caused to periodically traverse

the bed or beds, and turn over the material to expose fresh surfaces; or, as in Brunton's calciner, the bed is horizontal, and revolves. Projections from the roof turn the material over, and gradually move it towards the edge, where it is discharged.

The McDougall, Wedge, and Herreschoff roasting furnaces consist of a series of circular hearths, Fig. 42, placed one over the other, which communicate with each other through openings alternately at the sides and centre. Each hearth is provided with rabbles attached to a central shaft rising through the middle of the furnace and capable of revolving at varying speeds. The ploughs are set at an angle so as to direct the material to or from the centre as necessary, so that the ore falls from bed to bed in passing through the furnace. The upper bed often takes the form of a drying platform. Wear on the ploughs through overheating in contact with sulphur—always great in a closed furnace—is diminished by water cooling the arms, or by admitting air to the furnace through the arms. (In mechanical furnaces where the ploughs pass outside the furnace, as in the Brown-O'Hara, the wear is less, as the ploughs are cooled by the air when outside the furnace.)

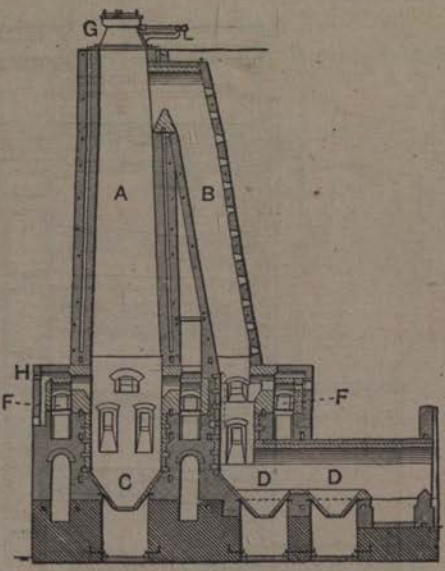


FIG. 41.—Stetefeldt Furnace. A, tower; B, descending flue; C, discharge door; D, dust-hoppers; F, fireplaces; G, feed hopper.

The diameter of the furnace varies from 12 to 16 feet. The ore is fed from a hopper. A fireplace or oil-burner is provided, so placed that the flame and hot gases enter the furnace at the second or third bed. The main excess of sulphur is removed on the upper beds, and the higher temperature necessary to continue the calcination is derived from the fire heat. Air enters at the bottom of the furnace, and passing over the heated ore carries part of the heat back to the furnace.

In the **Spirlet roasting furnaces** used for calcining zinc blende the beds are alternately fixed and rotating. No ploughs are used, and the ore is turned over by firebrick projections, under each bed, which dip down into the charge on the bed below. Each bed is iron encased, and the motion is communicated from the *outside*. The moving beds being carried on roller tracks only about four horse-power is required to operate it. The bottom bed only is heated. No stack is provided, the gases passing off under a few tenths of an inch water pressure. The joints are luted by the fine material forming the charge. A final temperature of some 800° to 900° C. is reached, and the sulphur contents reduced below 1 per cent. without the formation of zinc ferrite. The latter interferes with the solubility of the oxide formed.

Electric Furnaces are largely used where electrolytic reduction, or very high temperatures, are required and where cheap power is available. They are used in the manufacture of aluminium, of carbides such as carborundum, Aitchison graphite, chrome, tungsten,

and other alloys for steel making, in making and refining special steels, and in iron smelting. Many types of furnace are in use,

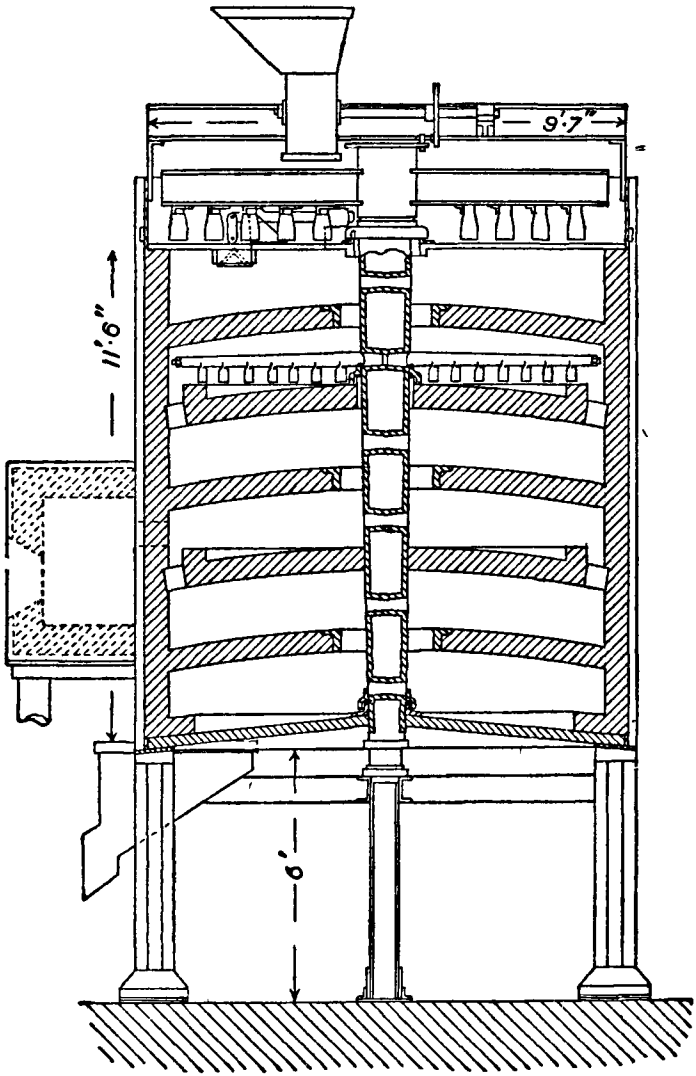


FIG. 42.—McDougall Calciner with oil heating.

mainly differing in the manner in which the current is employed to generate heat. They may be classified as follows :—

Induction Furnaces, in which the charge lying on the furnace bed or in a crucible constitutes the secondary coil of an induction unit,

and the induced currents produced by making and breaking the primary circuit, heat up the material. These are of limited application. The Kjellin, Ajax Northrop and Ajax Wyatt furnaces are of this type. See p. 203.

Resistance Furnaces.—In these the heat is generated by resistance in the circuit.

The resistance may be—

(*a*) The materials forming the charge, which becomes self-heating

(*b*) Rods of imperfectly conducting material embedded in the charge, and which become intensely heated.

(*c*) The body of the furnace itself may be made of resistant material, and become heated by the passage of the current.

(*d*) Small furnaces, such as tube furnaces, may be wound with wire of low conductivity and heated externally by heat generated by a current passing through the wire. Platinum, nichrome, chromel, and similar materials, are used for wire. The latter is safe to 1100° C.

Arc Furnaces.—The heat is generated by electric arcs. Temperatures of over 3000° C. may be attained. Carbon electrodes are employed to carry the current, and the arc is struck between them and the charge. Furnaces with a capacity of from two tons upwards are in use. They are used in steel manufacture, and also for smelting purposes. Both stationary and tilting furnaces are employed. The Héroult, Girod and Hall furnaces are of this type. The electrodes may pass through the roof, or by special arrangements through the side of the furnace (see p. 202).

The **structure of a furnace** may be divided into two parts: that portion which gives support and stability, and the portion specially adapted to resist the heat and the action of fluxes and slags. The latter constitutes the *lining* of the furnace chamber. The outer supporting part generally consists of common brickwork or masonry, often strengthened by iron bands, supported by iron plates (buck plates, from "buckle," "to bend"), and strengthened at intervals by thick iron plates or flanges (buck staves). These are fastened together by means of iron rods across the furnace—tie rods—to prevent accident from the expansion and contraction of the masonry. The outer masonry should be badly conducting material.

Special types of heat insulating bricks are sometimes employed for the outer brickwork. These are often of a porous or cellular character. The air cavities render them bad conductors of heat. They are used to prevent loss of heat by radiation, by keeping the outer walls cooler.

CHAPTER IV

REFRACTORY MATERIALS

THE substances employed for lining furnaces are required to withstand high temperatures and the corrosive action of such substances as they come into contact with in the furnace, and to possess in certain cases other important characters.

Fire-clay.—The most important and most generally used material is *fire-clay*. These clays consist mainly of hydrated silicate of alumina, $Al_2O_3 2SiO_2 2H_2O$ (alumina, silica, and water), with an excess of silica, and are marked by the small amounts of lime, magnesia, oxide of iron, potash, and soda which they contain. From the remarks on fluxes (see p. 45), the effect of these substances on clay, in producing fusibility, will be at once apparent.

No silicate of alumina is quite fusible at furnace temperatures, and when excess of alumina or silica is present the body is even more refractory. Analyses of various clays will be found below.

The water of hydration present is in chemical combination, and cannot be removed by drying at the boiling-point of water. Its presence in the clay gives to it one of its most important properties, viz. that of taking up water mechanically mixed with it, and becoming soft and plastic. Clay does not take up the maximum amount at once, but only gradually, so that previous to use clay is tempered with water and mellowed by exposure. The water taken up mechanically *can* be removed by drying. If not mellowed, the articles made from it are less tough and break more readily.

When clay is burned, the water of hydration is expelled, and a hard *anhydrous* substance remains. This body has no power of taking up water and becoming plastic, and no artificial means are known of restoring the clay to its original state. The expulsion of the water and fritting resulting from the fluxing effects of the impurities present during burning cause clay to contract, and allowance has to be made for this. In bricks, blocks, slabs, and other articles of simple form, this is done by merely making the dimensions of the body just large enough to allow for the contraction.

This, however, cannot be done in the case of crucibles, retorts, and other fire-clay ware. Owing to the unequal contraction of parts of different thickness, they would crack or become distorted in shape while being burnt, and thus rendered useless. In these cases, it becomes necessary to wholly or partly counteract the contraction.

This is effected by mixing with the clay substances which either do not contract, or which actually expand when heated. To the former class belong burnt clay (vermed grog), coke-dust, graphite, etc.,

and to the latter class silica, sand, and flint. Ground flint is principally used in pottery. A common mixture for making clay crucibles and retorts consists of two parts by measure of raw fire-clay or a mixture of various clays, and one part of ground crucibles, etc., or other burnt fire-clay.

ANALYSES OF FIRE-CLAYS, ETC.

	1.	2.	3.	4.	5.	6.
Silica	46·6	46·32	63·3	69·25	98·31	89·04
Alumina	39·5	39·74	23·3	17·9	0·72	5·44
Potash	—	—	—	—	0·14	
Soda	—	—	—	—		
Lime	—	0·36	0·73	1·3	0·22	0·31
Magnesia	—	0·44				0·17
Ferrous oxide	—	0·27	1·8	2·97	0·18	
Ferric oxide	—					2·65
Water, etc.	13·9	12·67	10·3	7·58	0·35	2·3
	100·0	99·8	99·43	99·00	99·92	99·91

1. $Al_2O_3 2SiO_2 2H_2O$. 2. China clay. 3. Stourbridge clay (Tookey). 4. Newcastle fire-clay (Richardson). 5. Dinas clay (rock) (Weston). 6. Sheffield ganister.

Fire-clays should be as free as possible from iron pyrites, FeS_2, as this body heated in air yields ferric oxide (Fe_2O_3), which, in contact with reducing agents such as the fuel, is reduced to the lower oxide FeO. This rapidly attacks the clay, forming at the point fusible complex silicates, and the surface becomes pitted, or even covered with a dark-brown slag.

The presence of organic matter is a common occurrence, as these clays are generally the under clay of coal-seams. They are usually hard and rock-like, with a somewhat soapy feel. Bituminous matter colours them grey.

Fire-bricks, besides being refractory, must be strong and of uniform size. The refractoriness is ascertained by making a test piece from the clay, the edges of which are kept as sharp as possible. This, after careful drying, is strongly heated, and, after cooling, the edges examined. If they remain perfectly sharp, the clay is refractory up to the temperature at which it was heated.

Any softening is evidenced by the rounding off of the edges, and glazing of the surface.

Firebricks should be burnt at the highest temperature to which they will be subjected in use, otherwise much trouble may develop. Bricks which contract may endanger the furnace structure or, as in coke ovens, cause the joints to gape and permit gases to escape. In by-product coke oven flues this may produce enormous losses of volatile matters.

The resistance of fire-clay to fluxes varies with its composition and character. The efficiency with which it is mixed and mellowed prior to use exerts considerable influence on the tenderness or otherwise of the bricks made from it.

Size is an important item in the usefulness of the bricks. If not uniform, much thicker joints will be required in setting them. These **joints** are the **weakest part of the lining**, the material used for setting is not consolidated like the material of the brick, consequently the thinner they can be made the longer

the lining will last. Fire-bricks are set in good fire-clay, and not in ordinary lime mortar. The action of lime, if used for this purpose, is obvious. It would combine with the clay at high temperatures, and flux it off—literally run away with the lining.

Ganister.—This substance is a highly siliceous body, as will be seen from the analysis. It is a kind of sandstone in which the grains are cemented by clayey matters, so that, when ground down and moistened with water, it binds together by pressure. Its chief peculiarity is that on burning, it neither expands nor contracts to any great extent. This permits of the lining being formed and burnt in the furnace itself. The moistened material in the form of coarse powder is rammed in between the shell and a wooden core, which is then withdrawn, and the lining gradually heated up. It is used thus for lining the wind furnaces for melting crucible steel, and the Bessemer converter. It is also used for patching up fire-brick linings. The absence of joints, and the great refractoriness of the body, make these linings very durable. Ganister is also made into bricks. It occurs in the coal measures.

Silica and Dinas Bricks.—The fire-bricks thus known are much more refractory than ordinary fire-bricks, so far as withstanding heat is concerned. As seen from the analysis, they consist mainly of silica. The materials from which they are made differ in character. Dinas bricks are made from a quartzite, and silica bricks from a more granular material of similar composition. The materials are crushed and mixed with 1 to 3 per cent. of milk of lime. This mixture is moulded in iron moulds having a false bottom, with the aid of pressure. After careful drying, they are fired at a very high temperature for several days. During the firing, the small quantity of lime added unites with the silica, etc., at the *surface* of the particles only, and frits or fuses according to the temperature, thus forming a cement, in which the particles of infusible silica are embedded.

Note.—The quantity of lime added does not affect the fusibility of the general mass. Its action is restricted to the surface of the particles.

Dinas bricks break with a coarse hackly fracture, in which the milky particles of quartz can be distinguished from the yellow matrix in which they are embedded. Silica bricks have a coarse granular fracture, and feel harsh to the touch.

These bricks are tenderer than fire-bricks, and should be protected from moisture. In moist situations they may disintegrate due to the action of the water on lime silicate. They *expand* strongly when heated, and hence their application is restricted to those positions where this can be allowed for, or provision made to prevent mishap.[1] Their principal applications are for constructing the ports and roofs, etc., of regenerative furnaces, and roofs of reverberatory furnaces. Consisting as they do of silica, they are unsuited for those parts of a

[1] The amount of *reversible* expansion varies from 0·6 to 1·25 per cent. linear, the *non*-reversible expansion from 0·1 to 0·6 per cent. Quartz on heating to high temperatures passes successively into tridymite and cristobalite at about 1,000° C. and 1,570° C. respectively. Silica bricks may contain both forms. Quartz softens considerably about 1625° C. and melts to a thin liquid at 1750° C.

furnace which are in contact with basic and highly corrosive materials or slags. (See Basic Lining.)

Sand is extensively used for making the bottoms of furnaces. The sand employed for this purpose is highly siliceous. It is used for the bottoms of regenerative open-hearth steel furnaces, and for copper-smelting furnaces. In use it becomes impregnated with metallic oxides, and forms a firm durable lining. Certain sandstones were formerly employed in blocks for the hearths of blast furnaces. The practice is now abandoned, owing to the tendency of blocks of natural stone to crack by heat.

Soap-stone and serpentine are used in Styria and Carinthia for lining the blast furnaces. These substances are hydrated silicates of magnesia, and are highly refractory. They abound in those neighbourhoods. In Sweden that part of the blast furnace which is subject to the strongest heat is lined with a mixture of crushed quartz and clay.

The materials hitherto considered, it will be observed, are of a **siliceous** or **acid** character, and in virtue of their chemical nature are unsuitable for certain purposes, as, for example, where heated for a prolonged period in contact with metallic oxides, which flux them away. Another and more important case, is in making steel from pig iron containing *phosphorus*, in the open-hearth and Bessemer processes. In the purification of iron, phosphorus is removed by oxidation as phosphate of iron or lime—a compound of phosphoric acid and iron oxide or lime—in the slag. These compounds are decomposed by silica, which combines with the oxide of iron, forming silicate, and separating the phosphoric acid, which is immediately reduced, and the phosphorus returned into the iron. It thus becomes impossible to remove phosphorus in a furnace lined with siliceous materials. As more than two-thirds of British irons contain too much phosphorus to be used for steel-making in acid-lined furnaces, its removal is a matter of the greatest moment. This can be effected by replacing the acid—siliceous—lining with a **basic** one, *i.e.* a lining consisting of metallic oxides.

In modern copper bessemerising a basic lining is employed to avoid the fluxing effect of the oxide of iron resulting from the oxidation of the iron in the matte.

Few natural basic substances are available, either from scarcity and consequent high cost, or from lack of refractoriness. They are devoid of binding power.

Among metallic oxides, lime (CaO), magnesia (MgO), alumina (Al_2O_3), and chromic oxide (Cr_2O_3), are most refractory.

Melting-points of refractory oxides and silica :—

Magnesia	2800° C.
Lime	2570°
Alumina	2050°
Silica	1750°

Lime, when exposed to the atmosphere, absorbs moisture, forms the hydrate CaH_2O_2, and falls to powder. Its application is, there-

fore, very limited. It was employed in blocks for the fusion of platinum by the oxy-hydrogen blowpipe.

Magnesia is free from the drawback of absorbing moisture, and the heavy dense form, obtained by strongly calcining magnesite, the natural carbonate of magnesia, forms an excellent lining material, $MgCO_3 = MgO + CO_2$. It is, however, devoid of binding power, and hence something must be employed as a cementing body. Its principal use is for forming the bottom of basic open-hearth furnaces, for lining basic Bessemer converters and electric furnaces. For the former purpose, the strongly calcined magnesite is either (1) ground down to a coarse meal, and then mixed with a small quantity of slag from the furnace, previously ground as fine as flour, and the mixture introduced into the heated furnace in layers, when the slag softens and agglutinates the mass: the quantity of slag is not sufficient to affect the refractoriness of the whole (compare manufacture of Dinas bricks); or (2) the material may be employed in the same manner as dolomite (see below). It is also made into bricks by the addition of a binder. These bricks are used in the lining of basic open-hearth and electric furnaces.

Magnesite lining is sometimes packed in thin iron tubular casings, which are built up to form the sides of the furnace. The iron becomes magnetic oxide by oxidation.

Dolomite.—The amount of magnesite available is small, but, fortunately, the property of not absorbing water applies not only to magnesia, but to the mixture of lime and magnesia obtained by calcining dolomite (mountain limestone). This consists of carbonates of lime and magnesia, and when strongly calcined, the carbonic acid gas is expelled, and a mixture of lime and magnesia remains, which is not readily affected by atmospheric moisture. This substance is largely employed for the purposes stated above, and is commonly known as the **basic lining.** The material is produced in the densest form possible by calcining at about the melting-point of iron, with blast and hard coke, so that the maximum shrinkage takes place before its employment in linings. It contracts about 50 per cent., and loses nearly as much in weight. Like magnesite, it has no binding property, and is used by mixing the coarsely ground material with from 10 to 15 per cent. or less of *well*-boiled tar, into a more or less adhesive mass, something like asphalte. This mixture, known as "slurry," is rammed into position with heated rammers, round a heated iron core, in Bessemer vessels, and in the bottom and sides of the Siemens furnace. On heating the lining, the tar is decomposed, or coked, and the carbon remaining cements the whole more or less firmly together. In use the lining becomes firmer and less porous by impregnation.

The mixture is also made into blocks for lining Bessemer converters. For this purpose a hydraulic press and steel moulds are employed. These blocks follow the curvature of the vessel, and are used in an unburnt condition. Clay, soluble silicate, etc., have also been used as binding agents. The introduction of this lining is due

to the energy of Messrs. Thomas and Gilchrist. It has been used in copper-refining furnaces to promote the removal of the arsenic from the metal and diminish loss, lime and magnesia replacing copper in the slag. The most suitable composition for practical purposes, which shrinks least, is stated by the above workers to be—

Lime	52 per cent.
Magnesia	36 „
Silica	8 „
Oxide of iron and alumina	4 „

Much of the dolomite in use contains less magnesia than is here shown.

Pure **alumina** is known as *corundum* and *emery*, substances whose other properties as gems (ruby, sapphire) or as grinding materials, on account of hardness, enhance their value, and preclude their use as refractory materials.

Bauxite.—A mixture of hydrated alumina and ferric oxide, however, occurs, and is known as *bauxite* (from Beaux in France). Its composition is very variable; the alumina ranges from 35 to 75 per cent., the oxide of iron from 2 to 38 per cent., and the water from 10 to 30 per cent., while silica is present in quantities of from 1 to 15 per cent. On heating, bauxite contracts and the water is expelled. This material is made into bricks by mixing it, after calcining, with a little clay and some graphite or coke-dust. The clay binds the mass together, and, when burnt, the coke-dust probably partly reduces the F_2O_3 to FeO, which combines with the alumina and forms a highly infusible aluminate of iron, thereby increasing the tenacity of the brick. These bricks have been used successfully in the bottom of basic-steel furnaces, for the lining of Siemens's rotary furnaces, and to form a parting between the basic dolomitic bottom of a furnace and the silica brick sides.

If these are in contact, the lime and magnesia in the lining and the slag attack, flux off, and undermine the side walls (see Fluxes), with the result that the furnaces collapse. By separating them by a course or two of bauxite bricks this is avoided. Being basic, they are not themselves attacked, and their dense character and composition prevents their attacking the bricks above. Hence the term **neutral course**, which is applied to this parting. Bauxite bricks are also used to line mechanical furnaces for various purposes.

Instead of bauxite, **chromite** is sometimes employed for this purpose. This is a mixture of oxides of iron and chromium, and is very refractory. It is employed in the same manner as dolomite, being either made into bricks or rammed in. Its use has extended to copper matting furnaces and Bessemer converters.

Oxides of Iron.—Besides the above basic materials, various substances, consisting mainly of oxides of iron (Fe_2O_3 and Fe_3O_4), are employed in making the bottom and sides of puddling furnaces for the conversion of cast into wrought iron. They not only serve as a more or less effective protection to the furnace, but play a most important part in the purification of the iron, and will be best studied in connection with the process (see p 169).

[1] Sillimanite often mentioned in connection with aluminous refractories is a natural crystallised silicate of alumina containing 63 per cent. of Al_2O_3. Mallite ($3Al_2O_3 2SiO_2$) contains 70 per cent.

In smelting copper ores the iron oxide present often forms a deposit of magnetic oxide on the sides of the furnace and on the sides and bottom of the converter if basic lined.

Besides these bodies, others are employed in special cases. In cupelling lead, for instance, **bone-ash** (phosphate of lime) is employed. This body is refractory, and is not readily attacked by oxide of lead. It is also of an absorbent character. In Germany and elsewhere a mixture of **marl** (a clay containing much lime) and charcoal is employed for the same purpose, under the name of *braque*. **Portland cement** is also used. Bone ash is also used as a wash for ingot moulds in copper refining.

Of late years the lining of the blast furnaces used in lead and copper smelting, with siliceous and other materials, has been abandoned in favour of water-jacketed furnaces. The highly corrosive slags produced in these processes have little or no action on the water-jacketed iron. Water-cooled iron blocks are also often built into furnace structures, to prevent those parts which are subject to the most intense heat being unduly affected (see Fig. 69).

Plumbago (natural graphite), being a form of carbon, is quite infusible. Its principal use is in making crucibles, etc. The mineral, after grinding, is treated with hydrochloric acid, to remove the oxide of iron, then washed and mixed with enough clay to bind the material together, and give the necessary strength. Flaky graphite is best for the purpose. Blacklead crucibles contain from 25 to 50 per cent. of graphite.

Crucibles are more or less cup-shaped vessels of refractory material in which substances are melted. This is generally done in wind furnaces, the pots being surrounded by the fire, and when the contents are melted, the crucible is grasped by tongs and lifted bodily from the furnace, and its contents poured out or teemed. These vessels must therefore be

(1) *Refractory*, to withstand the necessary high temperature.

(2) *Tough while hot*, so as not to break in lifting out.

(3) Must not crack when withdrawn from the fire and exposed to ordinary temperatures, *i.e.* must be capable of resisting sudden and great changes of temperature.

(4) Must not be seriously attacked and corroded by the materials heated in them, or by the ashes of the fuel.

(1) and (2) depend on the materials employed for making the crucible, the second being generally secured by a judicious mixture of various clays. Usually a fluxing agent is present in small amount. This at the working temperature softens and produces toughness. At very high temperatures crucibles used for melting steel can be crushed to a considerable extent without fracture. (3) and (4) depend largely on the grain of the crucible; a coarse-grained crucible is less liable to crack than a fine-grained one. This applies also to the heating up of the crucible; with fine-grained pots the greatest care must

be taken. On the other hand, coarse-grained pots are more easily attacked by fluxes and fuel ash, so that these two properties do not attain a maximum in the same crucible.

In many forms of tilting furnace the crucible is of special shape and is fixed in the furnace. The contents are poured by tilting the whole furnace. This avoids most of the difficulties due to handling and sudden changes of temperature. It greatly increases the life of the crucible.

Three distinct varieties of crucible are employed—

Clay, or white pots;
Plumbago, or blacklead crucibles; and
Salamander, or annealed blacklead crucibles.

Clay pots are made from various mixtures of fire-clay, with the addition of grog (ground pots—see Fire-clay), coke-dust, etc., to counteract contraction.

Plumbago pots consist of a mixture of plumbago with sufficient clay to bind it together. They are largely used for the fusion of metals and alloys, being more refractory and less acted on than clay pots. Relatively, with proper use, they last three or four times as long as clay pots.

Salamander pots do not require the same careful and gradual heating as the other varieties. They consist mainly of graphite in coarse grains, and may be coated with glaze to prevent them from absorbing moisture. These crucibles can be introduced immediately into a hot fire without danger; the coarseness of the grain, the conductivity of the material, and the absence of moisture prevent cracking. Small ones are specially suitable for blowpipe furnaces working with air or oxygen.

Crucibles are made of various shapes, materials, and fineness suitable for different operations.

The triangular form is specially suitable in small sizes for melting down metals. The corners are convenient for pouring.

Circular shallow pots, such as the Cornish copper assay crucible, are suitable when roasting as well as when fusions are to be conducted. In copper assays the materials are roasted in the crucible in which they are subsequently fused.

Such pots are also convenient in separating and collecting by fusion substances whose specific gravities are not greatly different, or which do not become perfectly fluid. Pots for tin assay, etc., are of this form.

Deeper pots are preferable where these conditions are not required.

When boiling up of the contents is likely to take place, skittle pots are most suitable. The wide upper portion and contracted mouth prevent the contents from frothing over.

For lifting with basket tongs from the fire, a slight contraction of the top permits of the pots being grasped lower down, and lifted with greater safety.

Fluxing pots are made of highly aluminous clay. They are very smooth, and resist the action of such corrosive bodies as oxides of lead, soda, etc., for a considerable time.

Crucible-making.—Small crucibles are made in plaster moulds on a revolving head, or whirling table, somewhat after the manner of pottery. On drying, the clay contracts and loosens itself from the mould, is turned out, thoroughly dried, and afterwards kiln burnt.

Large crucibles are made by hand and machinery. The method of making these

pots for melting steel, at Sheffield is as follows :—A carefully tempered mixture of clays, ground crucibles, and coke-dust is made into lumps of the right size. One of these is placed in a conical iron mould (the flask) previously well oiled. This is provided with a false bottom, having a hole through the centre. A plug—the shape of the interior of the crucible—with a spindle fitting into the hole of the false bottom of the flask, to keep it central, is pressed down into the clay, by dint of hammering with a mallet, and twisting to and fro, or by mechanical means. The clay rises and fills the space between it and the flask. When finished, an attendant lifts the whole, and places it on an upright post somewhat smaller than the false bottom. The flask falls by its weight, and the crucible is lifted off and taken away to be dried; or, if the top is to be narrowed, this is done with a sheet-iron cone placed on it and worked to and from as it stands on the post. The crucibles, after drying, are first carefully heated mouth downward in an annealing oven, some ten or twelve hours being taken to raise them to dull redness. They are then placed, without cooling, on their stands in the fires. These stands are blocks of similar material about 2 inches thick. When fully heated, a handful of sand thrown into the pots fills up the hole, frits, and cements the pot to the stand.

Owing to the vitrification that has taken place large clay crucibles cannot be heated again with safety after being allowed to become cold. They are ground up, after breaking off adherent slag, and used in the manufacture of others, and, in admixture with other materials, for steel-casting sand.

Brasqued Crucibles.—For purposes where contact with siliceous matters is objectionable, crucibles are frequently lined with carbon by mixing lampblack with a mixture of equal parts of treacle and water to a stiff paste. This is rammed into the crucible until it is filled, and a cavity cut out, leaving a lining from $\frac{1}{8}$ to $\frac{1}{4}$ an inch thick, according to size. The crucibles are filled with charcoal, or closely covered and heated to redness, Starch, gum, or oil may be substituted for the treacle, and with large crucibles tar may be employed.

Magnesia or alumina linings may be employed where carbon would be objectionable.

Other Considerations.—In the application of refractory materials, considerations other than refractoriness are sometimes of importance.

(1) *Density.*—Obviously in most cases light materials having sufficient strength (crushing) will be preferred, *e.g.* the specific gravity of fire-brick is 2·25, that of chrome brick 3·5–4, and it will be of importance whether the bricks are bought by the count or by weight.

(2) *Crushing Strength when Hot.*—This varies greatly. Most bricks lose strength rapidly when strongly heated. Silica bricks show a greater tendency to crack and spall when rapidly heated or chilled than ordinary fire-bricks.

(3) *Conductivity.*—In some cases, as in bricks used in chequers, it is necessary to have the maximum conductivity to abstract the heat from the hot gases rapidly and to give it up rapidly to the gas and air passing to the furnace.

On the other hand, badly conducting bricks prevent rapid loss by radiation.

Porous bricks are the worst conductors, owing to the bad conducting power of the gases (air) filling the pores. Special insulating bricks of a spongy character are made for lagging purposes. The

conductivity of an ordinary fire-brick increases with the temperature, as the closing of the pores by expansion of the solid granules reduces the surrounding gas films to a minimum.

Thermal Expansion.—This is important, because in expanding the thrust ensures that the mass of brickwork moves bodily, but in contraction this may not occur, and cracks in the brickwork may be produced. This is especially important in such cases as the construction of flues in by-product coke ovens. Fire-bricks expand little or may contract slightly. Silica bricks expand strongly, see p. 58.

Certain kinds of iron and iron alloys are used as " pots " for heating articles undergoing annealing. Nichrome, see p. 345, is coming into use for this purpose.

Carborundum (silicide of carbon) mixed with an aglutinant is used to a small extent. It is a good conductor of heat.

Alundum (fused alumina), zirconia, and fused magnesia are also used for small refractories.

TABLE SHOWING PHYSICAL PROPERTIES OF REFRACTORY MATERIALS.

	Specific heat.	Thermal conductivity.[2]	Compression strength in lbs. per sq. in.
Firebrick	0·192	0·0034	1,050
Silica	0·191	0·0020	2,300
Chrome	0·174	0·0067	3,900
Magnesite	0·220	0·0071	4,800
Refrax[1]	0·162	0·0275	12,500
Carbofrax[1]	0·180	0·0243	14,700

[1] Carborundum refractories.
[2] Gram-calories per degree C., per cm. cube, per sec.

CHAPTER V

FUELS

HEAT, for practical purposes,[1] is produced by the combustion or burning of substances in air, or occasionally in pure oxygen. The substance burnt combines chemically with the oxygen, producing gaseous or solid compounds, which pass away to the flues, or, if solid, remain behind. The chemical force exerted in the act of combination appears as heat, and the amount generated is in some measure an indication of the stability of the compound formed.

Any substance which by oxidation is made a source of heat for practical application is classed as a fuel. Most substances, including all those commonly employed, such as wood, charcoal, peat, coal, coke, and gas, are derived, directly or indirectly, from vegetable matter, and may be described as **organic fuels.**

Other substances less generally regarded as such are, however, fuels in certain operations. In calcining iron pyrites (which contains 54 per cent. of sulphur) and other rich sulphides, say in a Brückner calciner (p. 52), when the operation is once started, the heat developed by the burning sulphur is sufficient to carry on and complete the calcination. In this case sulphur is a fuel. In the Bessemer process (p. 190) for making steel, cold air is blown through molten pig iron, and the impurities present oxidised out. Instead of being cooled by the air, the metal becomes very much hotter, chiefly by the oxidation of the silicon in the pig iron to silica ($Si + O_2 = SiO_2$). In the *basic* Bessemer process (p. 193), phosphorus takes the place of the silicon in the ordinary process as a heat producer ($P_2 + O_5 = P_2O_5$). The SiO_2 and the P_2O_5 pass into the slag in combination with metallic oxides as silicates and phosphates respectively. In these cases, silicon and phosphorus are the fuels consumed, and sufficient heat is produced to maintain the purified iron in a fluid state. Sulphur in "pyritic smelting" and aluminium in the Goldschmidt reduction process are fuels.

Sulphur, silicon, phosphorus, and aluminium may be classed as **inorganic fuels.**

Organic fuels consist mainly of carbon and hydrogen, with varying amounts of oxygen and nitrogen, together with more or less inorganic matter, which is left behind on burning, and which constitutes the ash. Carbon and hydrogen being the only combustible substances present, a consideration of them is of the greatest importance.

[1] Except in the case of electric furnaces.

When oxygen occurs in a fuel, it must necessarily be in combination with other constituents. Such part of the fuel as is *already* oxidised cannot be further employed to develop heat, since the heat is produced in the act of oxidation.

In considering the value of a fuel from its chemical composition, it will be therefore necessary to deduct from the carbon or hydrogen a sufficient quantity to combine with the oxygen present. It is usual to make this deduction from the hydrogen. When hydrogen combines with oxygen it forms water, thus—

$$\begin{array}{l} H_2 + O = H_2O \\ \textit{parts by weight } 2 + 16 = 18 \end{array}$$

or 1 part of hydrogen combines with 8 of oxygen to form 9 of water. Conversely, 8 parts of oxygen require 1 of hydrogen, and by dividing the percentage of oxygen in the fuel by 8, we obtain the amount of hydrogen with which it is combined. Thus, if the fuel contains 18 per cent. of oxygen and 5 per cent. of hydrogen, $\frac{18}{8} = 2{\cdot}25$ parts of hydrogen are combined with oxygen *in* the coal, so that only $5 - 2{\cdot}25 = 2{\cdot}75$ parts of hydrogen can be burnt. This is known as *disposable* or *available* hydrogen.

Calorific Power.—When substances unite chemically, the combination always takes place between definite proportionate quantities of the bodies, thus—12 parts by weight of carbon always combine when completely oxidised, with 32 parts of oxygen, and produce 44 parts of carbonic acid gas, or—

$$\begin{array}{l} C + O_2 = CO_2 \\ 12 \quad 32 \quad 44 \end{array}$$

It is equally true that a definite amount of heat is generated. This can be expressed numerically. In burning 12 parts of carbon in the form of purified wood charcoal, 96,960 units of heat[1] are evolved. In burning 2 parts of hydrogen, 68,924 units of heat are given out.

The **quantity of heat** produced in completely burning **1 part by weight of the fuel** is the **calorific or heating power of the fuel.**

TABLE OF CALORIFIC POWERS.[2]

Hydrogen	34,462	Carbon monoxide	2,403
Marsh gas (CH_4)	13,063	Sulphur	2,261
Charcoal	8,080	Olefiant gas (C_2H_4)	11,857
Graphite	7,797	Silicon	7,830
Diamond	7,770	Phosphorus	5,747

[1] A unit of heat is the amount required to raise unit weight (say 1 lb.) of water through unit temperature (1°). A British thermal unit is the quantity of heat required to raise 1 lb. of water through 1° F.

The unit weight of fuel and water must be of the same denomination; lbs. or grams of fuel must correspond with lbs. or grams of water. The thermometer used must also be specified since 1° F. is only $\frac{5}{9}$ of 1° C.

[2] The numbers given in this table are the units of water heated through 1° *Centigrade*. If in grams, gram-calories, and so on.

The calorific power depends to some extent on the condition of the substance. Compare the calorific powers of carbon as charcoal, diamond, and graphite, in the table given above. The difference is due to the different amounts of heat required to bring about the molecular changes taking place in burning, and by which the carbon assumes a gaseous condition in the products of combustion.

Carbon can burn in two stages first forming the monoxide CO, which may be further oxidised to the dioxide CO_2.

A comparison of the relative quantities of heat generated in the two stages shows them to be widely different—

$$C + O_2 = CO_2$$
$$12 + 32 = 44$$
$$+ 12 \times 8080 = 96{,}960 \text{ heat units.}$$
$$CO + O = CO_2$$
$$28 + 16 = 44$$
$$+ 28 \times 2403 = 67{,}284 \text{ heat units.}$$

The same amount of carbon entered into the reaction in each case. It follows that only

$$\underset{\text{Total Ht.}}{96{,}960} - \underset{\text{2nd stage}}{67{,}284} = \underset{\text{1st stage}}{29{,}676}$$

29,676 heat units are made available in burning to CO.

Hence the C.P. of carbon burning to CO is $\frac{29{,}676}{12} = 2473$, or less than $\frac{1}{3}$ of its total calorific power.

The importance of securing complete oxidation of the carbon in fuel economy is apparent.

In blast furnaces and other cases where owing to smelting or other requirements reducing conditions exist and carbon monoxide is produced, wherever possible, arrangements are made to burn the gas and utilise the heat for blast heating or steam raising. See p. 131.

The usual method of stating **Calorific Powers of fuel**, in heat units per unit weight, assumes that the fuel is the only burning body. If the fuel were supplied to the air—a condition almost realised in the use of dust fuel and oil-spray fuels—the comparison would be satisfactory.

In metallurgical work the reverse is almost invariably the case. The air is supplied to the fuel, and the burning of the fuel depends on the amount of oxygen supplied. Further, the amount of heat required to carry on a given operation under specified conditions of temperature and pressure is a fixed quantity. The rate at which the action—say fusion—can proceed depends on the rate at which the heat is produced and the completeness of the application of the heat generated. Fuel burning rapidly, depending on a satisfactory air supply, produces heat rapidly. The disposition of the heat depends on the working conditions, such as the type of furnace, depth of charge, and its nature and method of packing, etc. Some reactions are only possible at the highest possible temperatures. Others proceed more rapidly at nigh temperatures, and in such cases the temperature must be maintained.

Seeing that the air supply is the principal common factor for all bodies, it may be useful to compare the heating values on the basis

of the oxygen consumed in combining with equal amounts of oxygen.

$$C + O = CO \quad + 29{,}676 \text{ heat units}$$

$$C + O_2 = CO_2 \quad + 96{,}960 \text{ „ „}$$

$$H_2 + O = H_2O \quad + 68{,}924 \text{ „ „}$$

$$CO + O = CO_2 \quad + 67{,}284 \text{ „ „}$$

On the basis of combining with equal amounts of oxygen the ratios are—

$$29{,}676 : 48{,}480 : 68{,}924 : 67{,}284$$

ratios which are very different from those occurring in the table of calorific power.

In the case of hydrogen, another point must be noted. The product of combustion—water—is a liquid at ordinary temperatures. All calorific power determinations include the whole of the heat given out. In furnace gases the water exists as steam. To retain it in this condition heat is required. Each part of water requires 589 heat units,[1] and each part of hydrogen produces 9 parts of water. Hence $9 \times 589 = 5{,}301$ heat units will be rendered unavailable for heating purposes, and the 34,462 must be reduced by that amount. This gives the heating value of hydrogen as 29,161. Substituting this figure in the foregoing equations, the comparative figures become

$$29{,}676 : 48{,}480 : 58{,}322 : 67{,}284$$

respectively. For metallurgical purposes this gives a much more satisfactory comparison, since the nitrogen carried in the air blown in and which has to be taken into consideration is the same for each case, the unit of oxygen being taken as the basis.

The **net calorific value** of a fuel is obtained by deducting from the calorific value sufficient heat to retain the water produced by the burning of the hydrogen in the state of vapour.

Useful effect of Fuel.—The effectiveness of a fuel depends not only on the amount of heat developed, but also upon the disposition of the heat. In some cases the degree of concentration possible and the temperature attained are the most important considerations, as in the Thermit process. The calorific value of aluminium is less than that of carbon, but the concentration of heat is great because heat is not wasted in heating nitrogen, as is the case when the oxygen is derived from air, and, the product of combustion being a solid, no heat is carried off by the products of combustion, as is the case with carbon, the carbon monoxide or dioxide passing away heated to the temperature of the combustion.

[1] This is made up of the latent heat of steam (537) and the heat required to raise the water to the boiling-point (100° C.); note being taken of the difference between the specific heats of water and steam respectively.

The heat resulting from combustion may be distributed by (1) conduction, (2) radiation, (3) convection. In burning solids, the solid itself becomes heated by heat conducted from the burning surface, and glows more or less intensely, radiating heat in all directions. Substances in contact with it become heated by conduction. The amount of heat thus communicated by solids depends on the areas in contact. The major part of the heat communicated from glowing fuel is radiant heat. Only surfaces opposite each other can exchange heat in this way, so that the thinnest possible film of heated solid, if the difference in temperature be maintained, will transfer as much heat either by radiation or conduction as a thicker layer. For this reason, in crucible furnaces the layer of burning coke may be made as thin as possible consistent with the maintenance of a complete layer of glowing material between the furnace wall and the crucible. Control of the air supply ensures that a sufficient amount of heat is generated. For the same reason a coil of wire or foil wrapped round a furnace tube is sufficient to maintain the temperature so long as a current of adequate strength is passed through the wire. Radiation is mainly responsible for the transfer of heat between the glowing solid and the materials in the furnace.

When air is used to supply oxygen, or gaseous products of combustion are formed, the gases are raised to the temperature realised, and the heat produced is largely taken up by them. Thus, in a blast furnace they rise through the materials of the charge, or, in a reverberatory furnace, pass over into the furnace chamber. In this manner they carry the sensible heat away from the region of combustion and distribute it by convection.

It is most important to remember that gases are very poor radiators, and only become heated or cooled by actual contact with solid matter, *i.e.* by conduction. To secure effective interchange of heat between gases and solids, every effort must be made to ensure such contact.

It has been mentioned that gases are very bad conductors, so that dust or any cause that retains a stationary film of gas in contact with the solid will prevent the interchange. The efficiency of heating stoves and regenerators is largely affected by dust in this way.

Determination of Calorific Power.—The calorific powers of the constituents of a fuel being known, it becomes possible to calculate the calorific power of a fuel from its composition.

Example.—A sample of coal gave on analysis, carbon 75 per cent., hydrogen 6 per cent., oxygen 15 per cent., nitrogen and ash, etc., 4 per cent. The available hydrogen = hydrogen $- \frac{1}{8}$ oxygen $= 6 - 1{\cdot}875 = 4{\cdot}12$ and calorific power of fuel $= \frac{75 \times 8080 + 4{\cdot}12 \times 34{,}462}{100}$.

Calorific powers calculated from analyses of fuels are not reliable, as we have no knowledge of the manner in which the constituents of the fuel are combined.

Direct determinations of the heating power are consequently made. Instruments used for this purpose are known as calorimeters.

A weighed quantity of the fuel is burnt, and the heat generated is given up to a known weight of water, the temperature of which is previously ascertained. The temperature of the water is again taken after burning the fuel, and the number of degrees it has risen noted. Then—

$$\frac{\text{weight of water} \times \text{rise in temperature}}{\text{weight of fuel}} = \text{C.P.}$$

In the weight of water, allowance must be made for the heat absorbed by the vessel containing it, and other parts of the apparatus, and, for strict accuracy, for other minor losses of heat, such as the heat carried off in the gases as the temperature of the water rises, radiation, etc.

Fuel calorimeters are instruments for determining the calorific power. They may be divided into—

(1) Calorimeters in which oxygen is supplied to the fuel by some solid material such as chlorate of potash, potassium nitrate, or sodium peroxide.

FIG. 43.

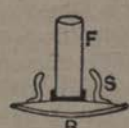


FIG. 44.

FIG. 45.

(2) Those in which oxygen is supplied as gas from a compressed supply and in which the gaseous products of combustion are allowed to escape freely through the water employed to retain and measure the heat.

(3) Calorimeters in which the oxygen is employed in a compressed form in a strong metal cylinder or bomb, and from which no gases are allowed to escape. The high state of compression used permits sufficient oxygen to be contained in a bomb of reasonable size.

In those calorimeters in which oxygen is obtained from potassium chlorate and nitre, or in which free escape of gases is permitted, much heat is carried away by the escaping gases, and error is bound to arise.

Thomson's Calorimeter is shown in Figs. 43, 44, 45. It consists of a glass vessel 12½ inches high and 4 inches wide, containing up to the mark 29,010 grains of water. The fuel to be tested, mixed with oxidising agents (see below), is carefully introduced into the copper furnace tube F. This is placed in the socket on the base B, which also carries three springs S, for the attachment of the cylindrical copper hood (Fig. 45). At the bottom of this hood is a circle of small

holes to allow the gases generated to escape, and a narrow tube terminating in a tap T, rises from the top. The oxidising mixture consists of 3 parts potassium chlorate and 1 part potassium nitrate. Two grms. of coal and 20 grms. of the mixture are used. An addition of 10 per cent. of the observed rise in T° is necessary to allow for loss of heat in the escaping gases.

The fuel is ignited by a short piece of lamp-cotton soaked in nitre, which forms a slow-match.

Fig. 46 shows the Roland Wild calorimeter, using sodium peroxide as a source of oxygen. In this case no gas escapes as the carbon dioxide produced is retained in combination with the sodium oxide as carbonate, and the moisture condenses in the crucible in which the combustion takes place. The fuel—0·73 grm.—is mixed with 12 to 14 grms. of sodium peroxide in a granular state, not too fine, to prevent explosion. The mixture is placed in the metal crucible A, 2 inches in diameter, which screws firmly into the cover C, attached to the pipe D, carried by the wooden cover E, as shown. The pipe D is closed by a ball valve F, or a tap.

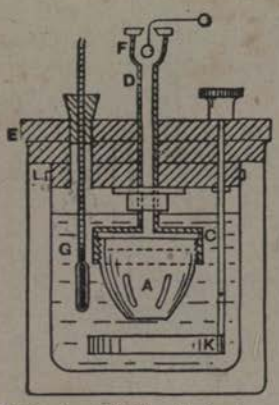


FIG. 46.—Wild's calorimeter.

The calorimeter vessel G, $5\frac{1}{4}$ inches deep by $4\frac{1}{2}$ inches diameter, contains 925 grms. of water, and is carried by a bayonet joint from the wooden cover, resting on the outer casing L, which is empty and serves as a lagging for the calorimeter. A thermometer passes through the wooden cover, and is immersed in the water. K is a stirrer to secure uniform temperature.

The temperature of the water is read, and the fuel ignited by dropping a piece of nickel wire $\frac{1}{2}$ inch long,[1] made red hot in a Bunsen burner, through the valve into the mixture, the valve being immediately closed. The stirrer is operated to ensure a uniform temperature, and the highest temperature attained read off.

The difference represents the rise in temperature of the water.

The water value of the instrument—about 75 grms.[2]—must be added to the weight of the water in the vessel.

Thus rise in temperature × weight of water = total heat. Of the total heat about 27 per cent. is produced by the combination of the carbon dioxide and water produced in burning, with the sodium oxide. By using only 0·73 grm. of the fuel, allowance is made for this, and the results are obtained directly with a Fahrenheit thermometer in British thermal units, and with a Centigrade thermometer in calories.

With the weights of water (925 grms.) and with a water equivalent

[1] Electrical ignition is attached to Wild's calorimeter in the newest forms.
[2] This should be experimentally determined.

for the instrument of 75 grms., the total water is 1000 grms., so that multiplication is easy and the instrument is direct reading.

Bomb Calorimeter.—The Mahler-Kroeker bomb calorimeter is shown in Fig. 47. A is the bomb, B the calorimeter, and C the outer casing containing water to prevent absorption or loss of heat. It also carries a means for operating the stirrer D in the calorimeter, and a support for the thermometer.

The bomb, Fig. 48, is a nickel-steel cylinder capable of withstanding a pressure of 300 atmospheres. The inside is coated with enamel. The gun-metal screw-cap carries means for electric ignition, and is provided with pin valves A, through which the oxygen is admitted and the gases finally escape.

The fuel—1 grm.—is placed in the capsule supported between

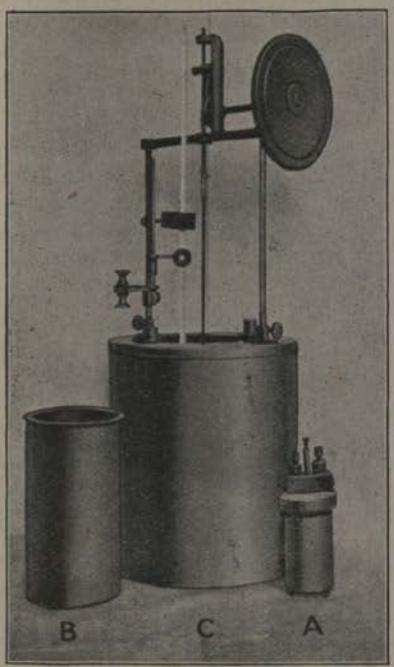


FIG. 47.

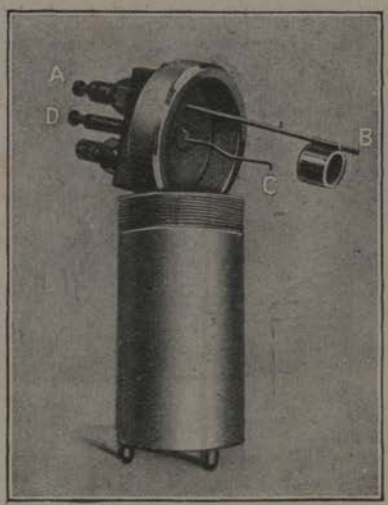


FIG. 48.

the oxygen tube B and the insulated post C. A short coil of very thin iron or platinum wire, which rests on the fuel, is attached to the post and tube respectively, at the ends. The cap having been screwed down tightly, oxygen is admitted from the oxygen cylinder to a pressure of 25 atmospheres. The electrical connections are made at A and D—but the circuit is not closed, and the bomb is placed in the water in the calorimeter, previously put within the jacket. The thermometer is put in place and the stirring gear attached.

Note.—The thermometer is a very delicate one, graduated to 0·01 of 1° C., which enables the figures of the third place to be obtained. If a Fahrenheit thermometer be used the results can be converted into Centigrade units by multiplying the result by $\frac{5}{9}$ and *vice versâ*.

The stirrer is set in motion and readings are taken every half-minute till a constant temperature is reached, then the circuit is closed, the fuel ignited, and the readings continued every half-minute till the maximum is reached, and further continued till the temperature begins to fall at a uniform rate.

Then, obviously, if t = rise in temperature
t_1 = amount of heat lost by calorimeter
W = wt. of water *in* calorimeter
w = water equivalent of calorimeter—specially determined
f = weight of fuel
h = heat evolved by burning iron

then $\frac{(t + t_1) \times (W + w)}{f} - h$ = calorific power (gross).

t_1 is obtained as follows: The difference in T° between the maximum and the final reading is divided by the number of periods. This figure multiplied by the number of periods (less 1) between the ignition and the maximum represent the heat lost by the calorimeter during the combustion and absorption. Half the period loss may be added for the first period—the temperature not having risen much during that interval. The water equivalent of the bomb is about 335, but varies somewhat, and should be determined. A useful amount of water in the calorimeter is 2200 grms. This just leaves the electrical connections clear.

THERMOMETER READINGS.

Prior to ignition.	Until the maximum T° has been reached.	After the maximum T° has been reached.
17·99° C.	18·04°	20·591°
18·005°	18·68°	20·583°
18·013°	19·58°	20·575°
18·013°	20·25°	20·567°
18·013°	20·51°	20·56°
	20·583°	
	20·598°	

Then correction for cooling—

$$20·598 - 20·56 = 0·038$$
$$\frac{0·038}{5} = 0·0076$$
$$(0·0076 \times 6) + 0·0038 = 0·049$$

and $(20·598 - 18·013) + 0·049 = 2·634°$ Rise in T°.

$$2·634 \times (2200 + 335) = 6676$$

less $0·02 \times 1500$ (iron wire) $\quad 30$

Calorific value $= 6646$ calories

or $6646 \times \frac{9}{5} = 11{,}962$ [1] B.Th.U.

[1] Coal gives from 12,000 to 16,500 B.Th.U.

Full descriptions of the bomb and its working will be found in Poole's "Calorific Power of Fuel."

Since the heat produced is wholly generated by the burning of the fuel, and is retained in the calorimeter, instruments of this type are the most accurate in use for the determination of calorific power. They may also be used for determining the calorific power of liquids and gases.

The *net* calorific value is obtained by deducting the amount of heat required to maintain the water generated by the burning of the hydrogen in the state of steam in the fire gases.

The *temperature* produced by burning a given fuel is dependent not only on the amount of heat given out, but on other conditions also: the *amount* and *nature* of the products of combustion, whether the combustion takes place in air or pure oxygen, the initial temperature, and the stability of the products of combustion. The temperature realised is below that calculated from the net calorific value, and the mass and the specific heat of the products, and is determined by the stability of the products of combustion, for, when a certain temperature has been attained, these may be dissociated as rapidly as formed, and the heat thus absorbed balanced by that given out.

In practice, the temperature, when burning solid fuel, depends on the rapidity of combustion and the density of the substance, assuming that the composition is the same. The more rapid combustion which attends the employment of hot air, as well as the heat carried in by the air, greatly increases the temperature, while the structure of the substances influences the rate at which it burns—porous cellular bodies burning most freely.

Dense fuels, when burning at the same rate as lighter ones, produce greater local heat, the heat-evolving and radiating power being concentrated in smaller volume.

Note.—The amount of ash in a fuel is important. Not only does it displace combustible matter, but in a blast furnace it must pass into and increase the amount of slag. Further, if infusible, suitable fluxes must be added, making more slag. This entails the use of more fuel to provide the necessary heat. Furnace space is occupied by all these extra bodies, thus reducing its output. Increase in the material increases costs of handling, and further adds to the charges the operation has to bear. Hence low fuel ash is desirable.

In other cases the presence of the ash increases the firing difficulties, as in cementation furnaces, although fine anthracite is sometimes burnt on a thick clinker bed broken up to permit the passage of air.

Wood is extensively employed as a fuel where a plentiful supply is obtained and high temperatures are not required.

The organic constituents of dry wood, exclusive of ash, are—

Carbon	51·0 per cent.
Hydrogen	6·0 ,,
Oxygen	41·5 ,,
Nitrogen, etc.	1·5 ,,
	100·0

Note.—The composition of various kinds of wood is almost identical, no constituent varying much more than 1 per cent. The principal body present in all is cellulose $C_{12}H_{20}O_{10}$, with various hydrocarbon substances, as turpentine, resins, etc., which influence its inflammability. Its density varies from 0·4 to 1·3. The large amount of oxygen will be at once noticed, and from what we have previously learnt, the disposable hydrogen is only $6 - \frac{41·5}{8} = 0·82$ per cent. All the water of composition, 41·5 + 5·18 = 46·68 per cent., has to be evaporated. This, added to the fact that ordinary air-dried wood retains from 15 to 20 per cent. of mechanically held moisture, which has also to be expelled, will show the unsuitability of wood for the production of high temperatures. If kiln-dried, it reabsorbs a great part of the moisture on exposure.

The ash of wood rarely exceeds 2 per cent. It is characterised by the presence of a considerable amount of potash and the absence of alumina. It consists of carbonate of potash, lime, soda, iron, magnesia, with a little chlorine, sulphuric and phosphoric acids, and silica. Wood ashes formerly formed the chief source of potash salts.

Wood has a calorific power of about 3,000.

The woods principally employed are: larch, fir, sycamore, birch, elm, ash, pine, and oak.

The inflaming point of wood is about 300° C., much below redness.

Charcoal.—When wood is gradually heated out of contact with air, it undergoes a destructive distillation. Water and various other volatile compounds are expelled, some of which result from decomposition of the cellulose and other bodies present in wood, with the separation of free carbon. This decomposition commences at about 180° C., and is completed at about 400° C. The residue obtained is charcoal. It consists of the *fixed* carbon of the wood, with the ash, and some hydrogen and oxygen, the amount of which depends on the temperature of preparation.

The substances expelled consist mainly of water, wood naphtha, various heavy hydrocarbons constituting tarry matters, marsh gas, hydrogen, olefiant gas, carbonic oxide, carbonic acid gas, pyroligneous acid (crude acetic acid), and ammoniacal compounds. The valuable nature of some, and combustible character of others of these substances, will be noted.

The weight of charcoal obtained varies from 15 to 25 per cent., rarely exceeding 20 per cent. Its volume is from 50 to 75 per cent. of the wood. The yield depends on the nature of the wood, the temperature, and rapidity of charring. High temperature and slow charring diminish the yield owing to the more complete distillation which occurs. Good charcoal should be hard, sonorous, give a bright fracture, not soil the hands, not friable or fissured, and retain the form of the original wood. Its igniting-point depends much on the temperature of preparation, as the higher the temperature the denser and less easily ignited it becomes. Rapid charring has the effect of making the charcoal fissured.

The combustible nature of the substances expelled by charring will show that, unless high local heat is required, it would be more economical to simply dry wood. The *quantity* of heat given out by

burning the wood itself is greater than that given out on burning the charcoal prepared from it.

Charcoal may be prepared in two ways. The wood may be charred in retorts heated externally by a fire, or it may be piled in a kiln or stack, and the charring effected by a complete or partial burning of the volatile matters which distil off when the wood gets heated, the preliminary heating being effected by faggots put in some convenient position in the pile.

When charring in retorts is followed the pyroligneous acid and tar may be collected, the charcoal being a by-product.

Charcoal Burning in Piles.—The piles are made either circular or rectangular. In circular piles, the wood, sawn into suitable lengths, is built up round a central stake or stakes, in the manner shown in Figs. 49, 50, and the pile covered with sods or earth, supported by branches, whose ends are stuck in the ground and bent

FIG. 49.

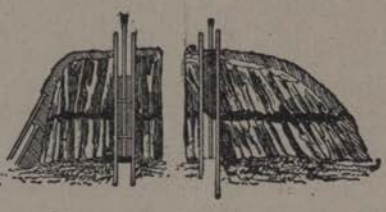


FIG. 50.

over, or, sometimes by a mixture of charcoal and water. This furnishes a yielding cover, but one sufficiently impervious to air as to exclude excess.

The charring of the wood is started by the ignition of faggots suitably placed in the pile and the supply of air carefully regulated by judiciously arranged openings made in the cover. These are closed when charring is complete in that region before burning of the charcoal begins. The gases exuding from the heated wood surround it and prevent contact with the air admitted.

The heat is maintained by the combustion of the volatiles inside the piles. If excess of air is admitted, the charcoal will be partly burnt. The quality is said to be improved by quenching it before it has cooled below its igniting-point. The quenching prevents burning of the charcoal, which might occur during the cooling if the stack were not tight.

Kilns are now largely employed, which ensure collection of the volatiles.

The amount of charcoal produced varies with the method of burning. It forms from 14 to 25 per cent. by weight, and from 50 to 75 per cent. by volume, of the wood. It absorbs about 10 per cent. of moisture on exposure to the air.

The specific gravity of charcoal varies from 0·11 to 0·2. If, however, air is expelled from its pores, it is found to be 2.

The **composition of charcoal** varies with the temperature of preparation. Ordinary charcoal, prepared between 400° and 1000° C., is as follows:—80 to 83 per cent. carbon; 1 to 2 per cent. hydrogen; 14 to 15·5 per cent. oxygen and nitrogen; 1 to 5 per cent. ash.

Peat, or turf, is produced by the gradual accumulation of dead vegetable matter, especially mosses and lower forms of vegetable life, in moist situations. The moisture protects it from the action of the air. Under these circumstances, a gradual change in its composition goes on. The oxygen and hydrogen in the original vegetable matters are slowly eliminated, as water (H_2O), marsh gas (CH_4), carbonic acid gas, etc. Up to a certain point the oxygen is removed in greatest proportion, the hydrogen in a less degree, and the carbon in the least proportion. The net result of these changes is that the proportion of carbon increases, the colour darkens, greater density is attained, and up to a certain limit the disposable hydrogen is increased.

These changes invariably occur when vegetable matter undergoes alteration in absence of air, and are assisted by even very moderate degrees of heat, such as the internal heat of the earth. The marsh gas, causing on ignition the will-o'-the-wisp, is produced in this manner. The fire-damp of the mine is also marsh gas, which has been stored in the coal under the pressure of the superincumbent material, and which, on opening up the seam, diffuses out of the coal. Carbon dioxide is more rarely met with owing to its solubility in water, which is always filtering through the rocks more or less.

The greater the degree of alteration the more widely it departs in character from the original vegetable matter. It is in virtue of these changes that coal, some of the varieties of which consist almost entirely of carbon, has been produced from the vegetable deposits of former ages. Under similar conditions, the greater the age the more altered the material becomes.

Peat usually occurs at the surface, filling up basin-like depressions. These are known as bogs, or mosses. It follows that *peat*, being of recent origin, is comparatively little changed, and that the upper and newest layer will differ from the lower and older layers. It will consequently resemble wood in chemical composition. On drying, peat from the upper part of a bog yields a light brownish-yellow fibrous substance, forming about 70 per cent. of the volume, and retaining sometimes over 30 per cent. of moisture after air-drying. Peat from the bottom of the bog is more gummy, and on drying yields a dense black compact mass, forming about 27 to 30 per cent. of the volume, and retaining about 20 to 30 per cent. of moisture after drying. The specific gravity of peat varies from about 0·1 to nearly 1; as taken from the bog it contains from 70 to 90 per cent. of moisture. The peat after removal is dried on floors, built in walls, and afterwards stacked or housed. This should be done in open weather, as frost seriously injures fresh peat. It never dries so firmly and dense after being frozen.

The preparation of peat, so as to produce from it a denser material more suitable for use as fuel, has received much attention.

Most of the methods adopted involve compression of the peat, either in a wet or air-dried state, into blocks. In others, the peat is converted into pulp by grinding. This, on drying, contracts to about one-fifth of its bulk, and yields a much denser material containing less moisture.

The **ash of peat,** as would be expected from the situations in which it is found, is much higher than that of wood. It ranges from 8 to nearly 30 per cent. It contains the same constituents as wood ash, with the addition of alumina. It contains, also, more of sulphates and phosphates, and often sulphides as well.

Peat commences to distil at about 130° C., and leaves a charcoal, the value of which depends on the character and amount of ash of the peat.

Fossil Fuels.—When deposits of vegetable matter have, by changes of level of the earth's surface, been submerged, and other strata deposited on them, the alteration previously noticed has continued, and the substance has entirely lost its vegetable character and become fossilised. The extent to which this has gone on depends on the age of the geological formation in which it is found, and sometimes on local influences.

Those substances which are found in the newer formations are called *lignites* (Lat., *lignum* = " wood "), from the distinct woody character of some of them, and those found in the older formation—known as the " Carboniferous "—are called *coal.* As would be expected, much difficulty is experienced in drawing a sharp limit between the two, as they gradually merge into each other.

Characteristic specimens, however, differ widely Selected examples of lignites and coals show a gradual passage from wood to anthracite (the most altered form of coal). Such a table is exhibited below. The striking feature of such an arrangement is that the available hydrogen gradually increases to a certain point, and the amount of fixed carbon—carbon not driven off in the volatile matters when the coal is heated—shows a similar increase.

The effect of this upon the character of the coal is important. The higher members of the series, in which the available hydrogen is low, burn without softening and fritting together, and if the powdered fuel is heated in a vessel from which air is excluded, the particles do not stick together. Such substances are described as **non-caking.** As the available hydrogen increases, the caking property becomes more and more strongly marked, until the substance becomes so rich in carbon as to again become non-caking, the bituminous matters produced during heating not being sufficient to bind the particles together. Thus the non-caking substances are of two classes: (1) those rich in oxygen, and low in available hydrogen ; (2) those rich in carbon

Fuel.	C.	H.	O.	N.	Ash.	Available hydrogen.	
Wood (desiccated) .	51·1	6·2	41·4	1·12	1·8	1·1	
Peat	51·38	7·03	40·59[2]			2·1	
(Coppage, Ireland)[1]							
Peat, Long (France)[1]	60·9	6·22	32·88[2]			2.3	
Lignite—							Non-caking.
Carolina, S. . .	60·3	4·8	20·2	1·0	3·2	2.3	
Auckland [2] . . .	64·7	4·81	18·25	1·34	10·48	2·53	
Tasmania . . .	69·14	5·4	18·48	1.26	5·37	3·1	
Trinidad . . .	75·63	5·2	13·51		2·64	3.5	
Coal—							
Cannel, Wigan .	80·07	5·53	8·1	2·1	2·7	4·5	
Andrew's House, Eanfield . . .	85·58	5·37	4·39	1·26	2·14	4·8	Caking.
Blaina	83·0	6·19	4·58	1·49	4·0	5·6	
Ebbw Vale . . .	89·78	5·15	0·39	2·16	1·5	5·1	
Aberaman . . .	90·94	4·28	0·94 O. and N.	1·21	14·5	4·1	Non-caking.
Anthracite (Isère) .	94·0	1·49	3·58 [2]		4·0	1·1	

Lignites.—Some of these are but little altered from woody matter. They are of a light colour and fibrous structure. These may be classified as *fossil wood*, or fibrous lignite. Such a deposit occurs at Bovey Tracey, in Devonshire. These lignites contain 30 to 50 per cent. of moisture, as won from the ground, and retain 12 to 20 per cent. after air-drying. On heating, they leave a residue of about 35 per cent.

Bituminous, or earthy, lignite is a convenient designation for those more altered in character. The colour is dark brown, the fibrous structure indistinct, and the fracture earthy. They contain less moisture than fossil wood.

The residue left on heating varies from 35 to 50 per cent., and 4 to 5 per cent. of tarry matters. Specific gravity 1·1 to 1·2.

The most altered lignites resemble coal in appearance, and to some extent in character. Some are black and shiny, others are dull, and black-brown in colour. The fracture is flat or conchoidal. All trace of woody fibre is lost. They contain less moisture, and leave a fixed residue up to 60 per cent. on distillation.

This class includes all the better varieties of **brown coal** (German, *Braunkohle*).

The volatile matters expelled from lignite resemble more or less those from coal, but are characterised by a large amount of aqueous distillate. The tars average some 4 to 6 per cent. Lignites are largely used in Germany, France, Italy, and Austria.

The ash of lignite consists mainly of oxide of iron, alumina, silica, and sulphates of lime and iron. It varies from 1 to 50 per cent.

[1] Exclusive of ash. [2] Inclusive of N.

The average composition of the organic constituents of the three varieties given below is from Regnault.[1]

	Carbon.	Hydrogen.	Oxygen and Nitrogen.
Fibrous lignite	63	5	32
Earthy	72	5	23
Pitch-brown coal	77	7·5	15·5

Coal.—Under this heading are included the more altered forms of fossil fuel. The term " bituminous coal " is applied to all those which burn with a more or less considerable amount of flame of a smoky nature, somewhat resembling pitch and bitumen.

Bituminous coal passes into anthracite, which burns without flame, smoke, or smell. Coals which burn rapidly, without softening and fusing together or breaking up into small pieces so as to arrest the draught, are described as **free burning.**

Caking Coals include all those which soften and stick together when heated. If the powder is heated in a closed vessel, a more or less coherent mass of coke is obtained. *Free-burning coals* are " non-caking," or only slightly caking.

As almost every coal-seam differs more or less from others, it is necessary to establish some method of classification.

Since the chemical composition of the coal affords little clue to its behaviour in burning, the most convenient classification is based on the amount and nature of the residue left, when the coal is heated in a closed vessel, minus the ash.

Coals containing a high percentage of oxygen or a very high percentage of carbon are non-caking (see p. 79).

Substances used exclusively for the manufacture of gas (boghead coal, etc.), or oils (paraffin coal), are not included.

Class 1.—Non-caking coals rich in oxygen (Percy). This includes the various kinds of *cannel*,[2] splint, or hard coal. They burn freely, with a long flame like a candle. (Cannels possess a dull pitchy lustre, break with a conchoidal fracture, give a brown streak, and are hard and dense.) The specific gravity is about 1·2. On heating, these coals retain their form, but do not cake together. The lumps of residue are cracked and friable. The percentage of coke varies from about 40 to 60 per cent; the fixed carbon present in the coke varying up to 53 per cent. of the coal. Cannels yield on distillation a larger percentage of volatile matters, and less coke than other bituminous coals. The ash and sulphur are also higher. Splint or hard coal was employed in blast furnaces in Scotland and Staffordshire.

The calorific power of these coals, *free from water and ash*, varies from 8,000 to 8,500. They occur in Staffordshire, Derbyshire, Lancashire, and Scotland.

[1] See Mills and Rowan's " Fuel."

[2] Cannels are supposed to have been produced in a different manner to coal. Some are caking in character.

Class 2.—Caking coal, burning with long flame—cherry coal (fat coals—Gruner). This class includes the various gas and many *steam* coals. These coals ignite easily, and burn freely, like Class 1, with much flame and smoke. They are very black and bright, and somewhat platey in structure, much more friable and not so hard as cannel, and are known as *soft coal.* Heated in a closed vessel, they coke slightly, some to a greater extent than others. The coke is light, spongy, and friable; it forms from 60 to 70 per cent. of the coal coked.

The gas is of good quality. They are largely used for manufacture of gas, and for steam-raising. The calorific power varies from 8,500 to 8,800. They occur extensively in South Wales and in the Newcastle, Staffordshire, and Glasgow coal-fields.

Class 3.—Caking or soldering coal—smithy coal. Coals of this class almost fuse when heated, and form a pasty mass from which bubbles of gas escape, leaving a coke altogether differing in form from the original. The flame is bright and luminous. The coals have a velvety black colour, generally soil the fingers, and have a tendency to break up into small rectangular pieces. They swell considerably during coking, and this reduces the density of the coke, which varies in quantity from 68 to 74 per cent. The calorific power is 8,500 to 9,300, but they are unsuitable for steam-raising, and many other purposes, owing to the great tendency to cake and impede the draught. They are largely used for the manufacture of coke. In Britain they occur in Durham, Yorkshire, Lancashire, Staffordshire, Derbyshire, South Wales, and other localities.

Class 4.—Coking coal (fat coal, burning with a short flame—Gruner). This includes those coals which, on account of the large yield and dense nature of the coke, are most suitable for making coke for use in blast furnaces. They are generally of a soft nature, liable to fall to pieces and crush. They ignite and burn less readily than preceding varieties, but do not soften and swell to the same extent. The flame is short, white, and almost smokeless. The coke is denser and stronger than from Class 3, and the yield from 74 to 82 per cent. It is the best for blast-furnace work. The calorific power is from 9,300 to 9,500. They are less suitable for steam-raising, unless forced draught is employed, than a freer-burning coal. They occur in South Wales, at St. Etienne, and elsewhere.

Class 5.—Non-caking coals rich in carbon (Percy), anthracitic coal. These coals gradually pass into true anthracite. They are harder, burn with little or no flame, are smokeless, and odourless. They ignite and burn with great difficulty, and, unless forced draught is employed perfect combustion cannot be ensured. Unless slowly heated, they crackle, fly to pieces, and impede the draught. Some kinds are less liable to do this than others, and in South Wales and Pennsylvania certain varieties were used for blast-furnace work. In appearance they are dull or streaky, and break with a more or less conchoidal fracture. The calorific power is somewhat less than

Class 4, as the hydrogen present is less. They leave an uncoked residue of about 82 to 88 per cent. They are employed as steam coals.

Anthracite is the most altered form of coal. It has a brilliant black or semi-metallic appearance, and gives a black streak. It is non-caking, and most difficult to burn, requiring a large draught. It is the densest of the coals, and generates an intense local heat. It is more liable to fly to pieces on heating than Class 5, bituminous coals. It burns without flame or smell. South Wales, Pennsylvania, and the Vosges are the principal localities. Anthracite leaves from 85 to 94 per cent. of fixed carbon, with less than 5 per cent. of ash.

The **specific gravity of coal** varies from 1·25 to 1·31. It is, however, influenced by the amount of earthy matters present. The **ash** ranges from 2 to 18 per cent., and consists of lime, alumina, oxide of iron, magnesia, alkalies, phosphoric, sulphuric, and hydrochloric acids, and silica.

The **sulphur** present in coal is of the greatest importance in the use of the material for iron manufacture in blast furnaces, as it is taken up by the metal. It exists in three states: (1) as iron pyrites—the brassy material in coal; (2) as organic sulphur; (3) as sulphate of lime, and sometimes of alumina. The two former states are most objectionable, *when used as coal* in iron smelting, as the sulphur, sulphuretted hydrogen, carbon disulphide, and sulphide of iron, which result on heating, may all transfer their sulphur to the metal. By previously converting the coal into coke, the organic sulphur is removed, and about half the sulphur in the pyrites.

To purify the coal from pyrites and dirt, for coking, forge, and other purposes, coal screenings are washed, the inorganic matter, in virtue of its greater density, separating from the coal. The specific gravity of pyrites is 5, nearly four times that of coal.

The pyrites present in coal often contains arsenic, and sometimes copper.

Phosphorus is generally only present in very small quantities. **Chlorine** is always present. It should not be overlooked in coals used for steam-raising in boilers fitted with copper tubes, which it rapidly corrodes.

The selection of a coal for any particular purpose depends as much on its physical as its chemical character. For blast-furnace work it must be hard and strong, not crumbling under the pressure of the charge, and it must not be too strongly caking. It must, moreover, be practically free from pyrites. Certain varieties of Classes 1, 2, and 5 of bituminous coal, and anthracite, are used for this purpose.[1]

In reverberatory furnaces working with draught, and for steam-raising, free-burning coal is employed.

For **technical** purposes, moisture, ash, fixed carbon, volatile matters, sulphur, and calorific power are usually determined.

Coke.—From the above consideration of coal, it will be seen that certain classes are not particularly suited for use in that form, either

[1] Coke has completely superseded coal for use in blast furnaces.

from their coking power, softness, or the presence of sulphur. These defects may be overcome by converting the coal into coke. Very soft coals often yield excellent coke, and, as before pointed out, half the sulphur in the pyrites present, together with the organic sulphur, is expelled during the coking, mainly as sulphuretted hydrogen and carbon disulphide. So that many coals unsuitable for iron manufacture yield coke which is not so prejudiced.

Coke stands to coal in the same relation as does charcoal to wood, and consists of the fixed carbon together with the inorganic constituents of the fuel. The percentage of ash in coke is consequently higher than in the coal itself (see p. 75).

When heated out of contact with air, coal splits up, yielding hydrogen, various volatile compounds of hydrogen and carbon, and of these elements with oxygen, ammonia, water, and coke. The heavier of the hydrocarbons, etc., constitute *tar*, and the water and ammonia, *ammoniacal liquor*. The lighter of the hydrocarbons are non-condensable, and constitute coal-gas. From tar, bisulphide of carbon, benzol, toluol, naphtha, creosote, phenol, anthracene, naphthalene, and pitch are obtained by distillation, at a gradually increasing temperature.

These substances are very valuable products. The composition of the tar, and the proportions of its constituents, will vary greatly with the temperature of coking. Low temperature favours the production of a tar low in benzol, toluol, carbolic acid, etc., and containing much heavy oily paraffin. A high temperature favours the production of tars rich in benzol, etc. These are much the more valuable. At high temperatures heavy hydro-carbons are decomposed, depositing part of their carbon, and being resolved into lighter bodies and hydrogen. This is often seen in gas-retorts, the inner surface of the retort, with which the gas has come into contact, being covered with a layer of dense carbon thus deposited. This is sometimes graphitic.

If the coal while coking can be sufficiently heated to decompose these in its mass, the coke obtained will be denser, stronger, and more brilliant in appearance. The yield of coke will also be greater, in proportion to the amount of carbon thus retained. It follows that the quality of the coke will depend not only on the nature of the coal, but also on the temperature of coking, and the rapidity with which it is attained, those processes producing the best coke in which the highest temperature is most rapidly obtained.[1]

As in charcoal-burning, the heat necessary may be obtained by partially or completely burning the volatile matters, in contact with the coal, or outside the coking chamber.

The combustible gases oozing out of the heated coal surround it with a protective envelope and prevent burning of the coke so long as they completely envelop it.

Coking in Heaps, Meiler, or Mounds was carried on in much

[1] This does not apply to coal which softens greatly on heating.

the same fashion as charcoal burning; the coal, which must be of a strongly coking character, being built into a circular heap round a central temporary chimney or disposed in long heaps or ridges. The amount of air entering the heap to burn the volatiles and heat up the mass was regulated by attending to the covering of earth, moistened coal dust, or coke dust which was applied at the beginning of the operation or put on when the escaping gases were no longer in sufficient quantity to envelop and protect the coke from burning.

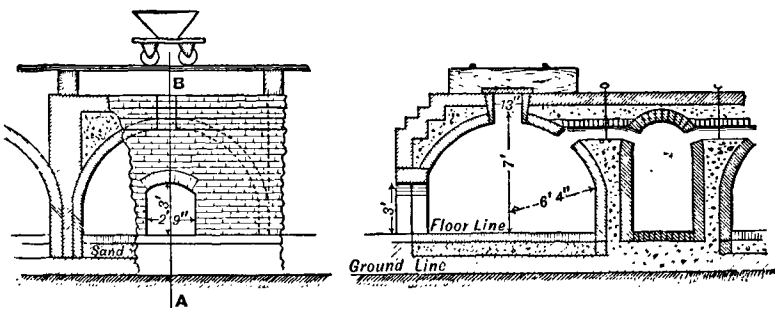
Coking kilns consisting of two parallel walls provided with suitable flues for regulating the air supply were also formerly employed.

Both methods are now completely superseded.

Coke Ovens.—Coke is now generally made in ovens, *i.e.* closed chambers.

They may be divided into—

(*a*) Simple chambers, to the interior of which air is admitted, to burn the products of distillation. Beehive, Rectangular.



Elevation part in Section. *Section through A.B.*

FIG. 51.

(*b*) Ovens in which the distillation products are *all* burnt outside the chamber. Appolt and old type Coppée ovens.

(*c*) Ovens in which the tarry matters and ammonia are removed by condensation from the gases, and the *non-condensable* gases burnt outside the chamber in flues—by-product ovens. The air supplied for combustion is now usually pre-heated. Simon-Carves, Semet-Solway, Bauer, Coppée, Otto-Hoffmann, Koppers, etc.

Beehive Ovens.—Many of these ovens are still in use. They yield coke of good quality, and can be employed with all classes of coal, whether it swells on coking or not, a consideration not to be overlooked. On the other hand, the yield is less than ovens to which air is not admitted, owing to burning of the coke, and much heat is lost and time wasted. The prime cost is, however, low, it costs little for repairs, and requires no large amount of skill. The chamber (Fig. 51) is circular, 10 to 12 feet in diameter, 2 feet to spring of dome, and 7 feet to the crown from the floor. The ovens are lined with refractory bricks, and are built in blocks of 40 or 50 on a double row, back to back, on a raised platform some 2 feet above ground-level.

The block is surrounded by a strong wall, and all spaces are filled up with sand or granulated slag to retain heat. A rail-track runs along the edge of the platform.

Each chamber is provided with a short chimney, or communicates by a short flue with a wide common flue, which runs between the two rows forming the block, and terminates in a stack.[1] The short flues can be closed by dampers, as shown. In front is an arched opening, some 3 feet high, which serves as a door for discharging the coke.

The coal is introduced through the top, from hopper waggons running on a rail track, and raked level.

The charging opening is covered, and the cover luted. In some cases the coal is shovelled in from the front.

The chambers are hot from previous charges. After charging, the front is loosely bricked up. If the oven is hot enough, the bricks are smeared over with loam to exclude air. If not, they are left uncovered for a time, and sometimes openings are made near the bottom to admit air. Distillation commences at once, but the gases are incombustible at the temperature of the oven. In from 1½ to 3 hours ignition commences, and the gases burn with a long, red, lurid flame, and much smoke. A small opening is then made in the top of the doorway to admit air *above the coal*, and burn the gases in the oven.

The temperature rapidly rises. The dome-shaped roof reflects the heat on to the mass of coal below, and this gradually gets heated through. The gases distilling off from below are partly decomposed in passing through the heated upper layers, and deposit carbon. The air-supply to the oven is regulated so as to burn the products *in* the oven as completely as possible without admitting any excess. When the distillation begins to slacken, the holes in front are stopped one by one, until the doorway is again completely closed. The chimney is also stopped, and the coke is left to itself some 12 hours to complete and cool. The doorway is first taken partly down, a hose-pipe introduced, and the coke quenched with water, in the oven, below its igniting-point. The door is then completely removed, and the coke discharged with rakes and forks. It breaks into columnar masses, the axes of which are vertical. This is owing to the direction of the coking, which takes place downwards. These ovens make from 3 to 5 tons per charge, and the yield is about 60 per cent.

The **rectangular oven** is exactly similar in principle, but the chambers are rectangular. The coking is conducted in the same manner. Sometimes the whole front of these ovens is open, and the bottom is made slightly sloping. It is then possible to remove the coke in one mass. For this purpose, before introducing the coal, a couple of strong iron drag-bars, turned up at each end, are laid on the floor of the oven, with the ends projecting, and the coal charged in on these. When the operation is complete, a windlass is attached to

[1] This flue gets intensely heated, and ensures combustion of the products of distillation. The hot gases are passed under boilers, to raise steam, before passing to the stack.

the projecting ends, and the whole mass dragged from the oven, being quenched as it comes forward on to the platform in front. The oven is thus left much hotter, and less heat and time are wasted.

In others, the front is arranged like a beehive, and sometimes an iron frame filled with fire-brick blocks, sliding in guides, and counterpoised, is used to close the mouth of the oven. Two charges a week can be worked off from each chamber. The coking itself occupies about 48 to 60 hours.

In the Appolt and old type Coppée coke ovens the coal was enclosed in brick-built chambers to which no air was admitted. The volatile matters escaped from the chambers by suitable openings into a surrounding space or into flues built in the walls of the chambers where they were burnt by the admission of a suitable supply of air. The walls of the chambers were thus heated externally. No air entered the chambers, and burning of the coke was avoided. By working the chambers in a suitable rotation and avoiding all losses of heat by providing facilities for rapid charging and discharging, the block of coking chambers could be kept hot and a high coking temperature maintained.

The chambers of the Appolt oven were vertical and those of the Coppée horizontal. A higher yield of coke was obtained. All the volatiles were burnt.

By-Product Coke Ovens.—In modern coking practice by-product ovens are almost universally employed. The volatiles distilling from the coal are conveyed from the coking chambers to condensing plant for the recovery of all the condensable products—tar and ammoniacal liquor—the non-condensable portion—coke-oven gas—being conveyed back to the ovens for combustion to provide the heat necessary to carry on the operation.

As previously noted, this removal of combustible matter diminishes the amount of heat available for the purpose and every means have to be taken to conserve the heat and use it in the most efficient manner to maintain a high temperature, the effect of which in influencing the quality and quantity of coke has already been noted.

With this end in view all modern coke ovens are provided with regenerators to preheat the gas and the air supplied for its combustion before admission to the flues in the walls of the chamber where burning is effected. The regenerators are heated by the waste hot gases leaving the flues on their way to the stack.

Ovens of this type consist of long horizontal chambers built in blocks with either horizontal or vertical flues underneath and in the side walls, variously disposed to regulate the circulation and direction of the hot gases.

In most cases the direction of the gases is reversed at regular intervals, separate regenerators being provided for gas and air in both directions, so that one set may be heating up while the other set is in use. This may entail the provision of four regenerating chambers

for each oven and elaborate arrangements to control the supply and the direction taken by the gases.

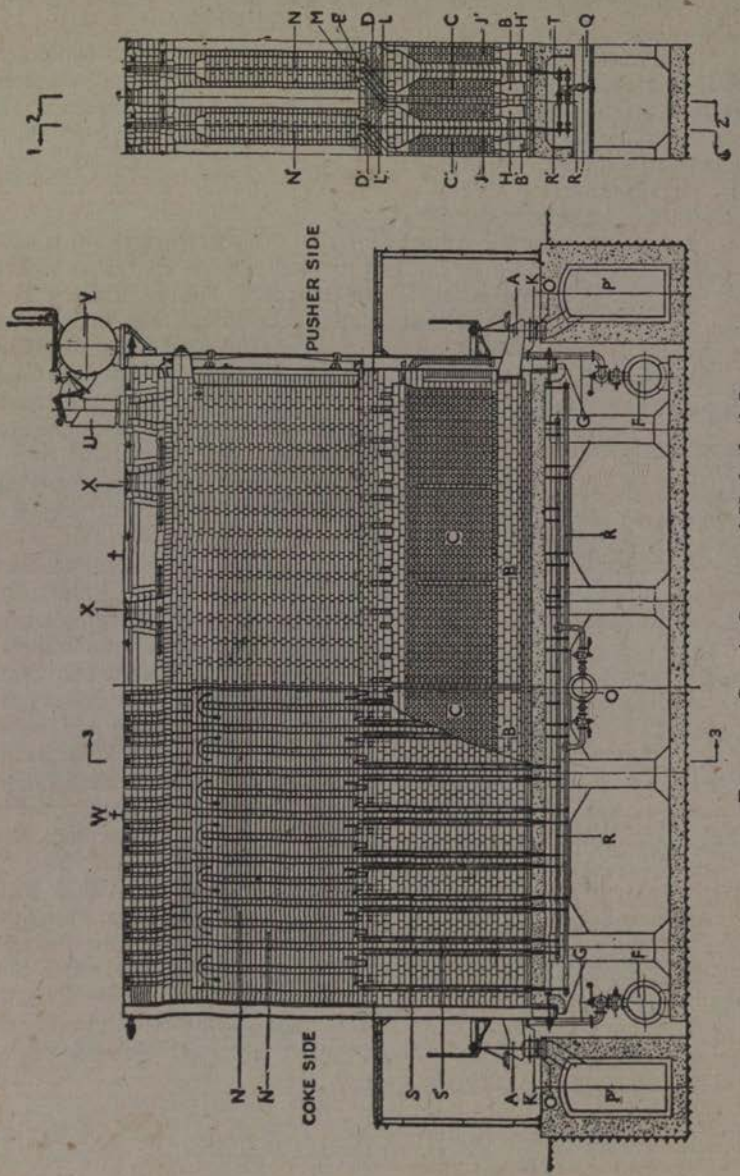


FIG. 52.—Coppée Compound Underfired Oven.

Figs. 52, 53, show the newest type of **Coppée** coke oven in section, and Fig. 53 is a photograph of a sectional model of the oven,

in which the various parts may be traced. The section of the model is through the coking chamber. The coking chambers are 40 feet long, 13 feet high, and from 16 to 18 inches wide. The side walls contain the vertical flues in which the gases are burnt. These are of the "twin" flue type (ascending and descending flues side by side), combustion taking place on the ascending side and as the gases return by the descending side of each flue to the regenerators under the

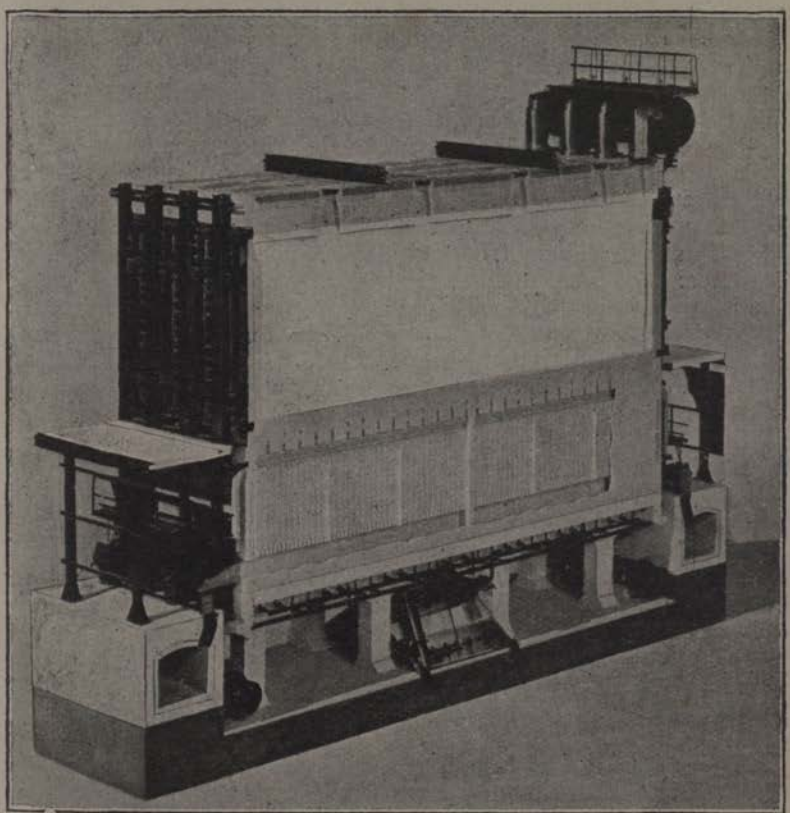


FIG. 53.—Model of Coppée Oven, showing distribution of parts. Section through Coking Chamber.

ovens. Like all modern coking plants, the battery of ovens is carried on arched or other supports that admit of free access to the means of controlling gas and air supplies and draught arrangements

Like most new plants, provision is made for using "rich" gas or "poor" gas: gas from which the condensibles have been removed.

Coal for coking is admitted through four openings, X, in the top, the charge being carried on a charger car running on the rail track W

and dumped simultaneously through each opening. The ends of the chamber are closed by self-sealing doors.

Gases are withdrawn by an exhauster through the opening U and the tar main V, and sent to the by-product plant. The "poor" gas is brought back to the ovens by the fuel mains F and distributed by pipes G through a compartment of the valve A and duct H into the regenerator J. A diaphragm K in the pipes G regulates the supply to the regenerators Similar pipes (G) for the supply of gas to J_1 are provided when reversal takes place. They are idle in the period as shown.

The gas preheated in the regenerator J passes through ducts L into the heating flues N. Dampers M over the distributing ducts L regulate the volume of gas required for each heating flue.

The air for combustion is drawn by the chimney through a second compartment in the valve A and through the duct B under the regenerator C. The air passing through the regenerator is distributed by the ducts D to the heating flues N. Dampers E are provided over the ducts D to regulate the supply to each flue.

Gas and air (preheated) meet at the bottom of the flue N and burn in the ascending flues N and return through N_1, the ducts D_1, and L_1 into the regenerators C_1 and J_1, through the ducts B_1, H_1, and the reversing valves A_1 to the main flue P_1 and chimney.

The suction on the regenerator is regulated by the damper O_1 at the point where the waste gases pass to the main flue.

On reversal the gases flow in the opposite direction.

When the ovens are heated with rich gas all the regenerators are used for preheating air, the chimney drawing air through both compartments of the valve A (which have adjustable openings).

The air enters the two chambers of each regenerator through B and H, and thence through ducts D and L to the heating flues N.

The rich gas is supplied by the main Q in the basement and distributed by pipes R and ducts S. The supply is regulated by diaphragms T. The ducts S and pipes T communicate with either side of the twin flues N to provide for reversal of direction. Combustion takes place and the burnt gases are removed through regenerators, as before noted.

In the period following reversal gas is supplied by pipes R_1 through ducts S_1 to flues N_1, and the flow of gases is in the reverse direction.

The cocks regulating the gas distribution are provided with slots to allow the passage of air into the gas ducts during the period when they are idle to burn off any deposit of carbon that might be present in the ducts.

In these and other ovens of the type, it is necessary to secure uniformity of heating both horizontally and vertically in the chamber with rapid development of and maintenance of high temperatures.

Uniformity over the length of the oven is secured by careful adjustment of air and gas to each flue.

The ends are apt to be cold owing to the vicinity of the door, and

produce "black ends," imperfectly coked material. This is obviated in some cases by providing a double gas supply for the end flues.

Uniformity in a vertical direction can be secured by regulating the rate of combustion in the flues. In this oven small division walls at the bottom of the vertical flues prevent the immediate complete mixing of gas and air and cause them to flow up in parallel streams, burning as they go. This prevents the production of a short intense flame with rich gas overheating the lower part, and by judicious adjustment allows the poor gas and air to mix sufficiently to burn steadily, otherwise as this gas burns with a long flame the top part of the walls would be overheated.

Ovens of the size 40 feet × 13 feet × 1½ feet will coke 24 tons of coal with 10 per cent. moisture per 24 hours if built of silica materials, and 20 to 25 per cent. less if built of fire-brick.

Great difficulty has been experienced with by-product ovens to secure tight joints in all parts of the system and prevent leakage of gas and air.

In modern practice the great progress that has been made in refractory materials has largely overcome this, silica and other refractories with the minimum change in volume, temporary or permanent, being employed. Special blocks and shapes are used to minimise the number of joints.

Care is also taken to ensure that uniform pressure conditions prevail so as to minimise tendencies to leakage.

In modern cokeworks the working conditions of the battery—fuel consumption, temperature, pressure, and calorific value of gas, temperature of burnt gas, chimney draught, etc., are all under control and recorded by meters, calorimeters, manometers, and other instruments.

In the **Becker** oven, instead of twin flues, the flues on each side of the oven are divided into six groups. The flues of each group communicate at the top and gather into a flue which conveys the gases over the top of the oven and down corresponding flues in the opposite wall, thence through regenerators to the flues. Reversals are carried out as in other ovens.

The **Kopper's** coke oven is shown in Fig. 54.

It consists of long narrow chambers built in blocks of 20–40. In the walls of the chamber are vertical twin flues which communicate at the bottom with common horizontal flues for the supply of air and gas, and removal of products of combustion in alternate phases.

The supplies can be regulated by nozzles at the bottom of each flue to secure uniformity of heating. Under each chamber are the chequer chambers for preheating purposes.

The supply flues are blocked in the middle, and gas is supplied from a main at each side of the block of oven as required. By operating a reversing valve on the regenerators, gas and air may be made to enter the flues at the bottom, at either end of the system, and, burning in the flues—each one acting like a bunsen burner—and so

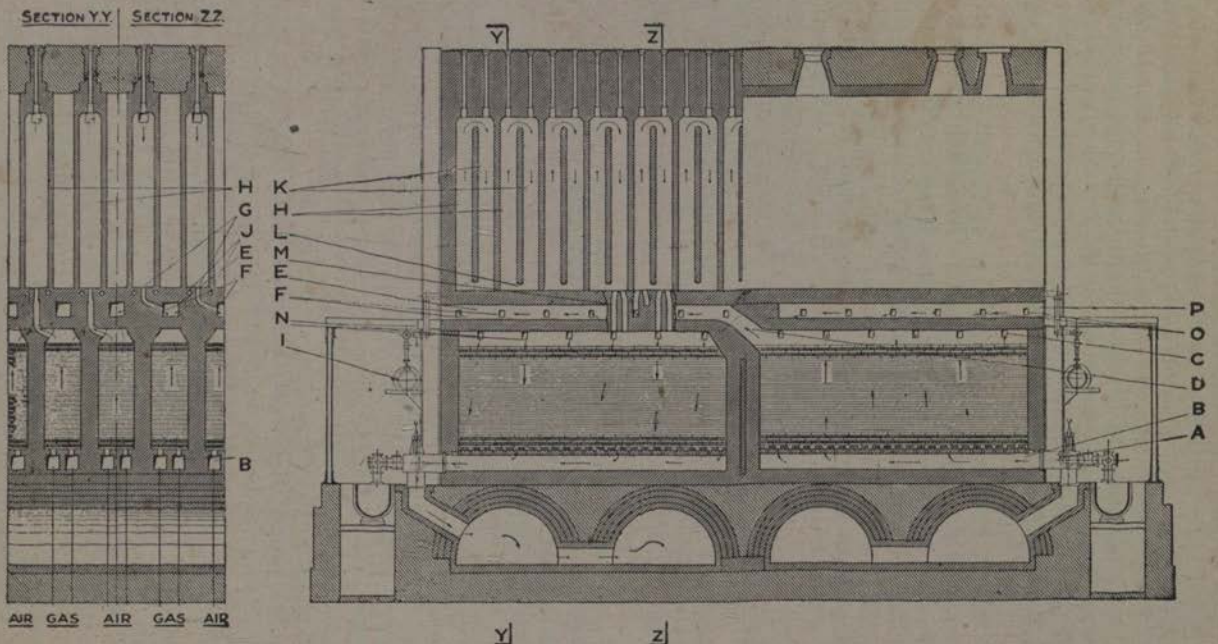


FIG. 54.—Kopper's Coke Oven.

to the generators and stack. A uniform high temperature can thus be attained and retained throughout the process.

The volatile matters are drawn off from the chambers by an exhauster, and after passing through a tar main, traverse the condensing plant before being sent back to the ovens.

Discharging.—When coking is completed the supplies of gas and air are stopped, the doors at both ends opened, and the coke removed by means of a mechanical ram which enters the chamber and pushes the coke out at the other side of the battery of ovens.

As it leaves the oven it is drenched with water to prevent burning —in most cases—a suitable water spray arch (or hose-pipe) being employed. In the former case the inner sides of the arch deliver water as the coke passes beneath it.

Note.—In the latest installations the coke is not quenched but is delivered hot into a receiving chamber where it is cooled by the circulation of inert—oxygen free—gases which absorb the sensible heat. These are carried away to boilers of special construction where the heat is utilised in raising steam. The system is a closed circuit, and the gases circulate round and round. Provision is made for the withdrawal of the cooled coke as required. It is taken straight to the blast furnace in conjunction with which the ovens are working.

The whole of the ovens being at work (on gas), the working is practically continuous, fresh coal being introduced immediately after the removal of the coke. In starting, it is necessary to heat the block of ovens to a coking heat by burning off a few charges without removal of tar, etc. The combustion of the uncondensibles, after this temperature has been reached, is sufficient to maintain it. The yield is 15 per cent. greater than the beehive oven, and the coke is of good quality, although not quite so dense and silvery in appearance. The period of coking may be reduced to as little as 12 hours. This compared with a probable production of two charges per week from the old beehive oven emphasises the progress in coking practice that has taken place and how the demands of the modern blast furnace are met. The coking is uniform, a high temperature being maintained throughout, and the character of the coke varies little on account of the thin slices in which it is coked.

In the **Simon-Carves** and **Semet-Solway** ovens, the flues are horizontal.

All ovens of this type are built of most refractory bricks. One of the main difficulties is the burning out of the flues.

Qualities of Coke.—Good coke should be—

(1) dense and compact;
(2) firm, not friable;
(3) uniform in character;
(4) as free from sulphur as possible; and
(5) should have good cell structure;

in order that it may burn freely, and develop great local heat under strong and hot blast, and not crumble and block the airways under the pressure of material above. The quality preferred by iron smelters

is that which has a strongly marked silvery appearance. Uniformity is important to secure regularity in burning.

Sulphur in Coke.—In coking, much of the sulphur in the coal is expelled as carbon bisulphide and sulphuretted hydrogen. Water thrown on red-hot coke causes sulphuretted hydrogen to be generated from sulphides it contains, and any one who stands near a mass of coke while being quenched will appreciate the offensive smell of this gas which prevails in the vicinity. The addition of salt, carbonate of soda, lime, manganese dioxide, and other bodies, has been made to the coal to be coked, with a view to retain the sulphur as sulphides not decomposed by iron, that is, in a form in which it would not pass into the metal smelted with it. These efforts are unsuccessful from various causes. Quenching has only a superficial effect, as the sulphides are only decomposed by water at red heat. Proposals have also been made to pass superheated steam through the mass while coking. As will be seen (p. 99), at a high temperature the coke itself decomposes the water, and a less yield is obtained.

. The coal screenings and ground coal used for coke making are generally washed in troughs, separators, or jigs to remove iron pyrites and earthy matters, and thus reduce the ash and sulphur in the coke obtained.

Coking of Non-caking Coal.—Coke may be produced from non-caking coal by mixing it with pitch, tar, etc., before coking, or by mixing it with strongly caking coal in suitable proportions.

CHAPTER VI

GAS FUEL

VARIOUS kinds of gas are employed for metallurgical purposes.

(*a*) *Towns Gas* (see analysis table). This is used mainly for heating crucible furnaces, and in small operations. The calorific value varies from 450–500 B.Th.U. per cubic foot. It is a rich gas.

(*b*) *Air* or *Producer Gas*, made by passing air containing more or less moisture through a deep layer of carbonaceous matter. The oxygen burns to carbon monoxide—the steam undergoes decomposition, producing carbon monoxide and some hydrogen. These together with the nitrogen of the air and small amounts of other gases dependent on the fuel used constitute producer gas. Various names are applied, *e.g.* Siemens, Wilson, Dowson, Suction gas.

(*c*) *Mond Gas*, the product of introducing the *maximum* amount of water vapour in the air supplied to the producer, see p. 99. It consists of carbon monoxide, carbon dioxide, hydrogen, and nitrogen, each in large proportions.

(*d*) *Water Gas*, made by passing steam through incandescent carbonaceous matter. It consists essentially of carbon monoxide and hydrogen.

(*e*) *Natural Gas*, consisting mainly of marsh gas (CH_4).

(*f*) *Blast Furnace Gas* (see p. 145).

The advantages of gas over solid fuel are—

1. More complete combustion can be ensured.
2. Better control of the temperature is obtained.
3. Greater uniformity of heating.
4. In regenerative furnaces—in which it is employed—a great saving of fuel takes place, and high temperatures can be more readily attained.
5. Better control is obtained over the atmosphere of the furnace, whether oxidising or reducing, etc.

Producer Gas.—When a limited supply of air is passed through a deep layer of incandescent carbonaceous matter, the oxygen is converted into carbonic oxide, CO. This, mixed with the nitrogen of the air and small quantities of carbon dioxide formed, and the products of distillation of the substance employed—hydrogen, hydrocarbons, etc.—constitute producer gas. Moisture entering with the air is decomposed, hydrogen and carbon monoxide resulting, which mix with and enrich the gas.

By this means the whole of the substance—fixed carbon as well as volatile matters—can be gasified, the only residue being, as in burning, the ash.

The composition of gas thus obtained varies somewhat according to the mode of production and nature of the material used. If the gas be cooled to remove water vapour, even wood sawdust, or any poor fuel, may be employed to produce high temperatures by combustion of the gas in regenerative furnaces.

Three types of producers are in use. The original **Siemens producer**, with a grate, in a modified form is shown in Fig. 55.

The fuel is contained in an arched chamber C, of the form shown, the bottom of which consists of fire-bars. Underneath is an ash-pit, A, closed by the folding doors D, through which the steam-jet blast-pipe P passes. The bottom of the ash-pit is a water-trough, in which the ashes are cooled, and the steam generated passes up into the producer.

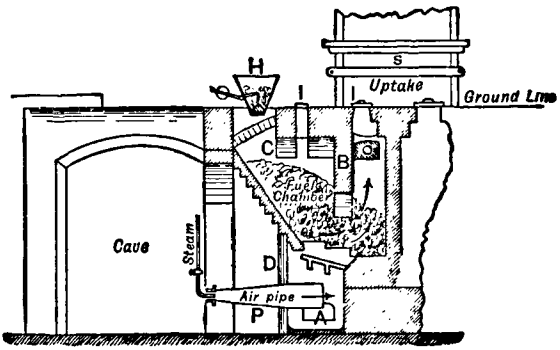


FIG. 55.

The gases pass off by the opening O into a vertical shaft S, called the "uptake." H is a hopper, from which fresh fuel is charged; I I are inspection openings, closed while working; and B is a bridge hanging down from the top, so as to prevent any air which may be introduced while charging from forming an explosive mixture by mixing with the gas without passing through the fuel. The top of the hopper is provided with a sliding door, which is shut before lowering the cone, to allow the fuel to descend into the chamber. The bridge also promotes the decomposition of the heavy tars by causing the products of distillation to descend through the heated lower portions. These chambers are usually built in blocks of four, and the uptake for the block is divided into four sections, each of which has a damper, so that any one of the producers may be stopped without interfering with the others. This type of producer is still used on R. Head's new type of Siemens furnace.

The **Wilson gas producer** is an example of the cupola type of gas producers, without a grate. It is cylindrical in form, and consists (Fig. 56) of an outer casing of iron plate, lined with refractory brickwork. The fuel is introduced from the hopper at the top, which is

provided with a sliding cover. The cone is counterbalanced. The bottom of the producer is of brickwork. A raised hollow ridge of brickwork crosses the bottom of the chamber, forming a flue.

The air forced in by the steam-jet S blowing into the mouth of the trumpet tube as shown, is delivered into this flue, and enters the chamber by the ports B on either side. Two cleaning doors, A, are provided for the removal of the clinker at intervals. While this is being done, the fuel is supported on iron bars thrust across the chamber through doors provided for that purpose, the steam being meanwhile shut off. In the upper part of the producer is a circular flue,[1] which communicates with the fuel chamber by the openings C.

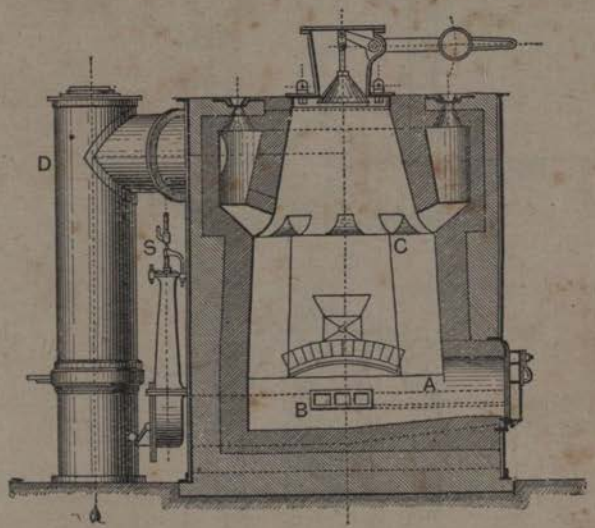


FIG. 56.

From this flue the gas is led away by the downtake D to the gas culverts. Openings round the top of the producer permit of the interior being inspected. The chamber is kept full of fuel, and, as the products of distillation must descend through the heated mass before getting away, the tars are largely decomposed.

Water bottom producers.—Modern gas producers are provided with a water seal closing the bottom. Fig. 57 shows such a producer.

This producer consists of an elliptical iron shell lined with refractory brickwork. The fuel is introduced from the hopper at the top, which is provided with a sliding cover, the cone being counterbalanced. At the bottom of the chamber a water trough extends towards the middle of the chamber and beyond the outer shell on each side of the producer. The edge of the casing dips below the level of the water

[1] In later producers of this type this flue is dispensed with.

to form a seal of sufficient depth to enable the necessary forced draught to be maintained. The air is introduced in the middle of the chamber, and the gas passes out at the side. As the carbonaceous matter is gasified the fuel ash accumulates on each side of the air inlets and forms the support on which the fuel rests. Ash is removed

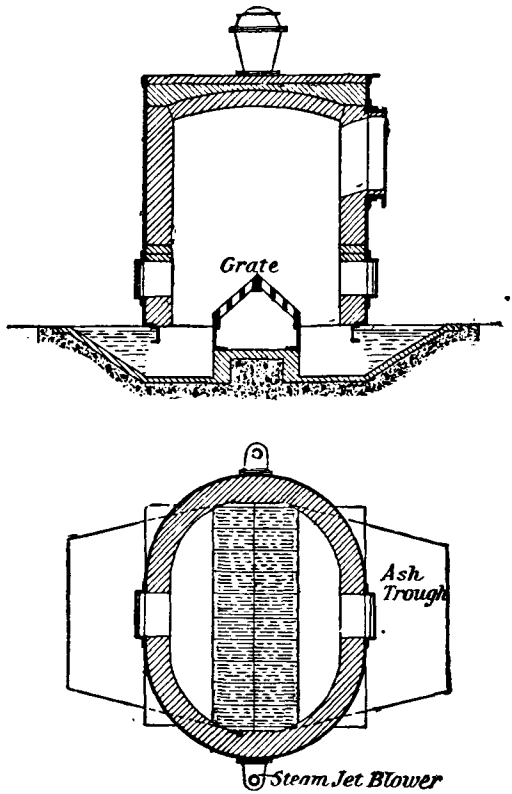


FIG. 57.—Water-bottom gas producer.

by means of a shovel with a long bent handle from the water troughs from time to time as may be necessary. In this way no stoppage has to be made to remove ash or clinker.

Heat that would be carried away by the ash if removed in the ordinary way produces water vapour which passes up into the producer. This action cools the ash in the burning zone and prevents the formation of objectionable clinker.

Modern gas producers are provided—

(1) with special water-cooled stirring apparatus to prevent caking of the coal (Morgan);

(2) rotary grates to prevent caking or to break up caked material (Kerpely);

(3) or may be water cooled, and built in sections which rotate slowly to secure the same results.

Fig. 58 shows a producer of the latter type.

Chemical Changes occurring in the Producer.—The coal or other material used undergoes destructive distillation, and the products mix with the gas. In producers using coal this may amount to approximately 5 per cent. of the total volume of gas. All the marsh gas is derived from this source.

The oxygen of the air forms carbon dioxide which is reduced to carbon monoxide in the upper layers of the incandescent fuel.

Any carbon dioxide that escapes reduction will be found in the gas produced. A sufficient depth of fuel—usually 2–4 feet—and uniform distribution of the charge will minimise the carbon dioxide escaping reduction. Irregular working, whether due to the caking of the coal, fusion of the ash, or any cause which permits the gases to pass upward without ensuring contact with the hot fuel, will lead to an increase in the percentage of carbon dioxide. It should not exceed 5 per cent. Carbon as carbon dioxide is completely burnt, and is consequently useless as a heating agent.

Nitrogen is not chemically affected in the producers.

It will be observed that in converting solid fuel into gas, part of the heat—that given out by the carbon in burning to CO in the producers—is lost unless the gas passes without cooling to the furnace. The great advantages derived from the use of gas, and the waste heat recovered in the regenerators, more than compensate for the loss, and a great saving of fuel is effected where high temperatures are required.

Where steam is admitted to the producer the heat generated by the carbon in burning to CO by combining with *free oxygen* from the *air* is utilised in decomposing the water vapour yielding free hydrogen and carbon monoxide. These gases on burning give out the heat absorbed in their production and thus carry forward in potential form much heat that would otherwise be dissipated and lost unless the producer gas could be transferred, without cooling, from the producer to the furnace.

If the quantity of heat available in the producer is insufficient to provide for the production of carbon monoxide (CO), more or less carbon dioxide will be formed to produce the heat necessary to decompose the water. The passage of unlimited quantities of steam would lead to such an absorption of heat that the temperature would fall below the ignition point of the carbon present and the producer fire would be extinguished.

The reactions may be expressed as follows—

$$C + H_2O = CO + H_2\,;\quad C + 2H_2O = CO_2 + 2H_2$$

the same amount of carbon being involved in each case.

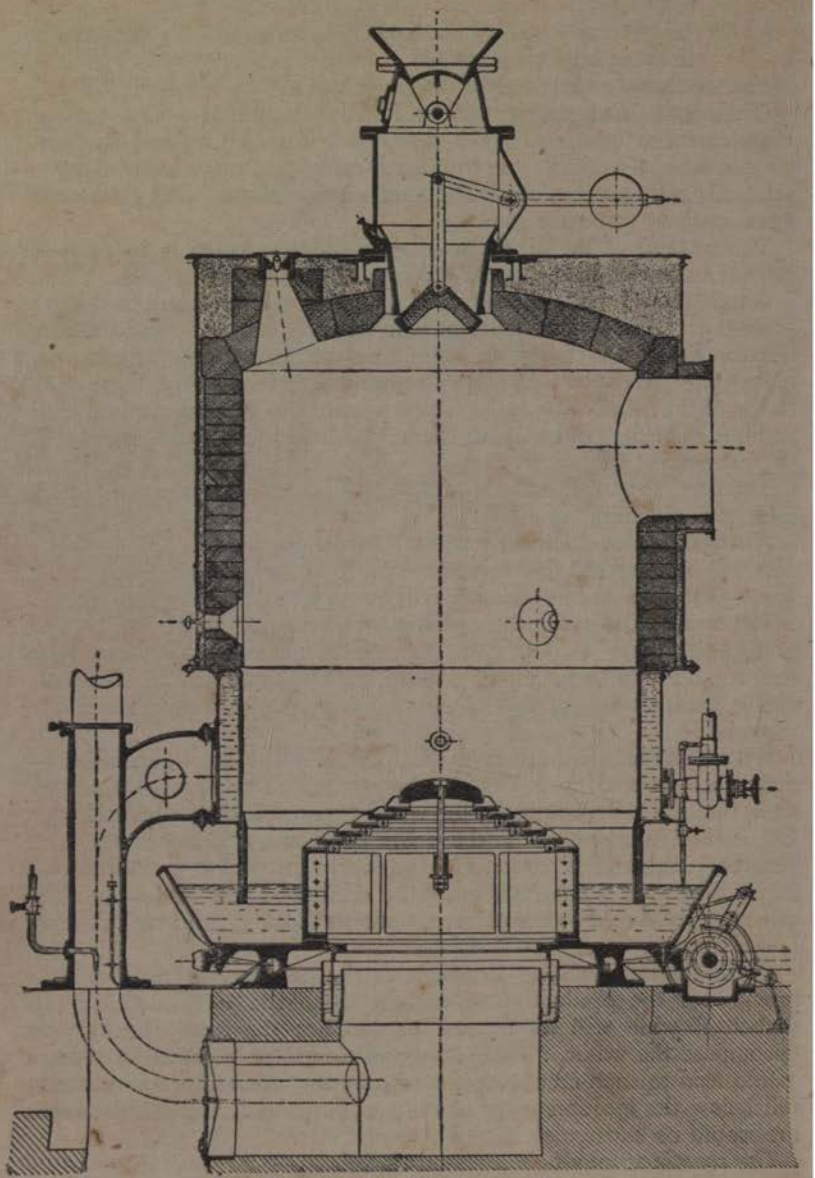


FIG. 58.—Producer with revolving bottom and water jacket.

The heat balances in the two cases are as follows—

$$C + H_2O = CO + H_2$$

	Heat units
The separation of the hydrogen from 18 pts. of water absorbs 29161[1] × 2 =	58,322
The combination of 12 parts C with O to form CO produces 2473 × 12 =	29,676
Loss in heat units	28,646

$$C + 2H_2O = CO_2 + 2H_2$$

The separation of H. involves absorption 29161 × 4 . . . . . =	116,644
The combination of 12 parts of carbon to form CO_2 produces . . .	96,960
Loss in heat units	19,684

From which it will be seen that the heat absorption in the two cases is approximately 2 : 3.

The heat required is furnished by the **sensible** heat stored up in the fuel in the producer.

This decomposition of water vapour leads to enrichment of the gas in combustible matter since the oxygen obtained from the water is not mixed with inert nitrogen and the hydrogen contents are increased.

In proportion to the amount of water decomposed it will be seen that less heat is absorbed when carbon dioxide is produced. So that producers may work at a lower temperature with a larger amount of water vapour, but the gas will be richer in hydrogen and in carbon dioxide. The carbon monoxide and hydrogen produced are the chemical equivalents of the heat energy absorbed, and by subsequently burning in the furnace reproduce the heat taken up from the producer by their formation.

In this way much of the heat *apparently* lost by burning the fuel to carbon monoxide in the producer is carried forward and reproduced in the furnace when the hydrogen and carbon monoxide burn. There is obviously a maximum amount of water vapour that may be used, viz. only as much as will utilise the surplus heat produced by the oxygen of the air blown in while maintaining the temperature of the producer.[2]

The gas obtained contains a greater proportion of hydrogen in place of carbon monoxide. The heating value of the two is not quite the same—

$$CO + O = CO_2$$
$$H_2 + O = H_2O$$

Here it will be seen that the same amount of oxygen is used to burn equal volumes of the gases. The thermal value of the burning carbon monoxide is (28 × 2403) = 67,284, and for the hydrogen (29,161 × 2)=58,322 by weight, and for volume per cubic foot at 0°

[1] Since the water is admitted as steam the *net* calorific value of hydrogen represents the heat absorbed. See p. 75.

[2] In ordinary producers practical tests show that the best results are obtained by using 5 to 7 per cent. of steam.

51901

and 760 mm. 152·5 (net) calories for hydrogen and 179 for carbon monoxide respectively.

The quantity of hydrogen converted to marsh gas (CH_4) is practically nil. Some sulphuretted hydrogen (H_2S) is generated.

The fuel generally is washed coal slack, but carbonaceous matter of any kind may be employed. The producers are generally at some distance from the furnaces, and the gas is conveyed to them in culverts. In some cases, the gas producer takes the place of the fireplace in a reverberatory furnace, as is the case with the Bicheroux and Boetius furnaces.

In Head's new furnace, arrangements are made whereby part of the CO_2 and other products of combustion produced by burning the gas is caused to pass through the producer. The CO_2 present is again reduced to CO. There is, therefore, a saving in fuel, the carbon in the CO_2 being used again. Heat is, of course, absorbed in its reduction. This is largely furnished by the excess of heat in the gases when they enter the producer. It would be impossible to return the whole of the CO_2 continuously for regeneration into CO to the producers. The proportion of nitrogen in the gas is unaltered.

Mond Gas is generated by passing into the producer air containing the maximum amount of water vapour that the heat produced is capable of decomposing. The temperature in the producer is reduced, and the reaction is principally—

$$C + 2H_2O = CO_2 + 2H_2$$

At this lower temperature a much larger proportion of the nitrogen in the coal is converted into ammonia, and the yield of ammonium sulphate in the recovery plant which forms part of the apparatus is considerable, amounting under the best conditions to 90 lbs. per ton of coal gasified.

Water Gas is a mixture of carbon monoxide and hydrogen, produced by passing steam through incandescent carbonaceous matter.

The decomposition of the steam and exclusion of nitrogen from the gas is effected by working the producer in an intermittent manner. The cycle consists of (1) "blowing hot" by first passing air through the tall column of fuel in the producer; (2) shutting off the air supply and blowing steam through the hot coke in the opposite direction.

Heat generated in "blowing hot" is stored and retained by the coke, which attains a high temperature. When steam is passed, the stored heat is utilised in decomposing the water vapour and the mass gradually cools, downward, as the heat is absorbed. When the temperature has fallen below decomposition point, steam is discontinued and the cycle beginning with the admission of air repeated. Producer gas produced in the 1st stage is applied in various ways in connection with the operation. In modern plants with regenerative appliances the periods of "blowing hot" and "steaming" are almost equal, approximating to 5 minutes.

Natural Gas consists mainly of marsh gas, and is given out in immense quantities in oil regions. It burns with only a faintly luminous flame. It is applied very extensively in Pennsylvania for furnace purposes. The supplies are said to be falling off.

COMPOSITION OF GASEOUS FUELS (by volume).

	Coal gas.	Siemens gas.	Wilson gas.	Blast furnaces gases.	Natural gas.	Water gas.	Mond gas.
Carbon monoxide .	7·82	24·20	26·44	26·29	2·0	44·4	11·02
Carbon dioxide . .	—	4·20	5·30	10.53	0·8	2·86	17·1
Hydrogen . . .	47·6	8·20	11·32	1·96	—	49·61	27·2
Marsh gas . . .	41·53	2·20	2·34	2·3	95·75	0·5	1·8
Other hydrocarbons .	3·05	—	—	—	1·45	—	0·4
Nitrogen	—	61·20	54·60	58·92	—	2·53	42·5
Percentage of combustible matters .	100·0	34·60	40·10	30·55	99·2	94·51	40·42

Calorific value (gross) per cubic foot at 62° F. and 30 in. mercury pressure—

H	325	British Thermal Units.	
CH_4	1005·3	,,	,, ,,
CO	322·2	,,	,, ,,
C_2H_4	1581·9	,,	,, ,,
C_2H_6	1757·6	,,	,, ,,

Oil Fuel.—Oil fuel is now extensively applied in the heating of large reverberatory furnaces. The oil is atomised by a jet of steam or air under pressure and sufficient air admitted to secure rapid and complete combustion.

In using oil fuel, or other fuel under pressure, the draught should be so regulated that only a very slight pull is maintained on the furnace, just enough to prevent the flame and hot gases escaping at the furnace doors, *i.e.* the chimney should be a duct to carry off the products of combustion rather than a means of creating draught for the supply of air.

Dust Fuel.—Pulverised coal is also employed for heating reverberatory and other furnaces, the dust fuel being carried forward by the air supply and burnt. In this way some of the advantages obtained by gasifying the coal are obtained without the employment of a producer, complete combustion being effected in one stage in the furnace. Obviously the ash is not excluded, and the preheating of the air offers difficulties. The use of dust fuel is increasing.

CHAPTER VII

IRON

THIS metal is employed in the arts in three forms: as cast iron, wrought iron, and steel of various kinds. Pure iron is a soft, greyish-white metal, very malleable and ductile, and highly tenacious. It is prepared by electrolysing a solution of iron and ammonium chlorides, sulphates, or oxalates, or by reducing precipitated ferric oxide by heating it in a current of hydrogen. Prepared thus at a low temperature, it takes fire spontaneously in air, but does not if prepared at a high temperature. After fusion, pure iron exhibits a crystalline, scaly fracture. It is softer than wrought iron, and is not affected by heating to redness and quenching in cold water. It is scarcely acted on by sulphuric and hydrochloric acids in the cold, but dissolves on heating. It is highly magnetic,[1] and welds readily. Its specific heat is 0·113, and its specific gravity 7·675. It melts at a lower temperature than platinum—about 1530° C. In mass it is unaffected by dry or moist air, oxygen, or water, if pure and free from carbonic acid gas. In the presence of this body it is readily attacked. At a red heat it is rapidly oxidised in air, yielding a scaly coating of oxide. Red-hot iron decomposes water, liberating hydrogen.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

When molten, it dissolves or occludes various gases in considerable quantities. Hydrogen, carbon monoxide, and nitrogen are thus taken up and given out on cooling.

The above physical properties are present in a greater or less degree in cast and wrought iron and steel, the extent to which they are modified depending on the purity of the substance.

These bodies consist of iron containing varying proportions of carbon, silicon, manganese, sulphur, and phosphorus, and occasionally copper, arsenic, tungsten, chromium, and other metals.

VARIETIES OF IRON IN COMMERCIAL USE.

Per cent.	Carbon.	Silicon.	Manganese.	Sulphur.	Phosphorus.
Pig iron	2–4·5	0·5–4·5	tr.–2[3]	tr.–0·2[4]	tr.–1·7
Ordinary castings .	2·5–3·5	1·0–2·5	tr.–1	tr.–0·15	tr.–1·7
Wrought iron . .	tr.–0·25	tr.–0·1	tr.–0·1	tr.–0·1	tr.–0·25
Mild steel	0·1–0·5	tr.–0·3	0·3–1·0	tr.–0·08 tr.–0·05	tr.–0·08[5] tr.–0·05[6]
Steel (ordinary carbon)	0·5–1·5	tr.	tr.–0·3	tr.	tr.
Alloy steels [2] . . .	0·3–0·7	tr.	tr.–0·5	tr.	tr.

[1] It cannot be permanently magnetised.

[2], [3], [4], [5], [6]: See footnotes on next page.

The above table is only intended to convey a general idea of the composition of the varieties of iron in actual use.

The ultimate analysis of a form of iron, *i.e.* the statement of the proportions of the elements present, does not indicate its real composition.

Carbon may be present in the free state or as carbide of iron, Fe_3C. In the latter form it will be seen that $(56 \times 3) = 168$ parts of iron are combined with 12 parts of carbon producing 180 of carbide. Thus 1 part of carbon produces 15 of carbide, and 1 per cent. of carbon in that form represents not 1 per cent. of a component or impurity, but 15 per cent. and *pro rata*. Similarly silicon forms mainly the silicide FeSi, each 1 per cent. of silicon representing 3 of silicide. Sulphur as FeS gives 2·7, and phosphorus as the phosphide Fe_3P, 6·5 (approximately) times its weight of sulphide and phosphide. It is in the form of their compounds which may be present that the effects produced by the impurities must be considered. A cast iron containing—

Graphite	2·5
Combined carbon	0·7
Silicon	1·8
Sulphur	0·15
Phosphorus	1·00
Total impurity as per analysis	6·15

would give

Graphite	2·5
Iron carbide	10·5
Iron silicide	5·4
Iron sulphide	0·4
Iron phosphide	6·5
Total impurity affecting the properties.	25·3

more than four times the amount formerly shown.

Iron and Carbon.—The great differences in the properties of cast and wrought iron and steel are mainly due to the presence of carbon in the metal, depending on the *amount* and the *manner* in which it exists in the iron.

[2] In addition alloy steels contain varying amounts of other metals, viz. tungsten (4–18 per cent.), chromium, manganese, molybdenum, vanadium, nickel, cobalt, silicon, aluminium, and occasionally other metals.

One or more of these elements may be present dependent on the purpose for which the steel is intended.

Rapid-cutting (self-hardening) steel may contain up to 18 per cent. tungsten, 4·5 per cent. chromium, 4 per cent. cobalt, 2 or 3 per cent. of molybdenum, 0·3–1 per cent. of vanadium. Nickel steels may contain up to 5 per cent. nickel, manganese steels between 10 and 13 per cent. manganese, and silicon alloys up to 4 per cent. for electromagnetic uses.

[3] In addition alloys—Spiegeleisen and ferro-manganese—containing up to 80 per cent. manganese are manufactured for use in steel manufacture. Similar alloys of silicon are also produced.

[4] Some irons made for special purposes, *e.g.* Raumur castings, contain more sulphur.

[5] For rails.

[6] For structural steel.

The maximum amount of carbon taken up by pure iron is stated by Riley to be 4·75 per cent. In cast iron containing manganese a little over 6 per cent. may be present. Steel may contain up to 1·8 per cent., while the carbon in wrought iron seldom exceeds 0·25, and may fall as low as 0·05.

Carbon may be imparted to iron—

(1) by heating it, embedded in charcoal, at a high temperature for a prolonged period ;
(2) by melting iron in contact with carbon, which it dissolves (see Cast Steel) ;
(3) by the decomposition of carbon monoxide, carbon being deposited and carbonic acid ultimately produced (though not by a simple reaction), as in the blast furnace ;
(4) by heating it in contact with gaseous or liquid hydro-carbons, such as paraffins, which are decomposed ;
(5) by the decomposition of cyanides, *e.g.* potassium ferrocyanide (yellow prussiate of potash), $K_4FeC_6N_6$, as in case-hardening or potassium cyanide KCN.

The iron combines with the carbon, forming a carbide having the composition Fe_3C, and the differences in the properties of the ferrous metals is mainly due to the amount and behaviour of the carbide present.

In molten iron the carbide dissolves freely and the carbon present in the metal in the fluid state is all in combination as carbide. The carbide is a stable compound so long as the amount present does not exceed the amount that can be held in solution by the metal. Just as the solubility of other compounds in solvents varies, the solubility of carbide of iron, in molten iron, varies with the temperature and other conditions. At high temperatures and also under special conditions *free* carbide of iron is unstable and decomposes into iron and free carbon.

When the carbide separates from iron during solidification it undergoes decomposition and the carbon assumes the flaky form of graphitic carbon. Any separation of carbide that occurs when the metal is solid may, if the temperature be high enough and conditions favourable, undergo decomposition, but the carbon separated cannot form distinct flakes, but remains distributed in fine particles—free but not flaky—through the metal. This is known as "**temper graphite.**"

Iron is capable of retaining 2·5 per cent. carbide, equal to 1·9 per cent. carbon, in solution when just solid. As the temperature falls some of the carbide may fall out of solution, but unless the temperature is maintained, decomposition does not occur. For this reason graphitic carbon is rarely met with in steels. The graphitic carbon existing in pig iron and castings renders them more or less grey in colour.

The extent to which separation of graphite occurs depends on the rate of cooling and the quality of the metal. Slow cooling, and the

presence of silicon and aluminium in the metal, favour the separation, while manganese retards it. When rapidly cooled, nearly all the carbon remains in the combined form, *i.e.* in solution as carbide. The properties of the iron are modified according to the *amount* and *manner* in which the carbon is held.

The carbide hardens the metal, lowers its melting-point, destroys its malleability and welding power, and tends to make it brittle. The extent to which these effects are produced depends on the amount. In white cast iron, containing as much as 3 per cent. carbon, *i.e.* 45 per cent. carbide,[1] the metal is brittle, breaks with a silvery-white fracture, melts more readily, and passes through a pasty stage in fusing. It is extremely hard, and this property is permanent. In *steel for cutting-instruments*, the amount varies from 0·5 to 1·5 per cent. carbon, 7·5 to 22·5 per cent. carbide. The hardness and fusibility are increased, the malleability and the welding power diminished in proportion to the amount of carbon present. In this case, however, the degree of hardness can be modified by special treatment without causing carbon to separate as graphite: heating to redness and slow cooling rendering the metal soft, while rapid cooling, such as quenching in cold water, etc., renders it hard. The degree of hardness can be modified by subsequently heating it to a lower temperature (see Tempering Steel). When hardened, the metal is brittle. The differences in hardness are due to changes in the manner in which the carbide is held and changes in the metal itself. The latter are influenced by the presence of carbide and also by other metals. The tensile strength and elasticity of steel are very high. It is magnetised with greater difficulty than pure iron, but *retains* its magnetism.

In wrought iron and mild steels, the carbon exercises an influence in the same direction in proportion to the amount present, but with small amounts the hardening effect is small.

Graphitic Carbon is met with only in cast iron, and occasionally in steel. It reduces the strength of the metal by interposition between the particles, and does not affect the grains of iron themselves. The amount of combined carbon may fall as low as 0·15 per cent., *i.e.* 2·25 per cent. carbide. Hence some very grey pig irons are exceedingly soft, and their melting-points very high.[2]

[1] Such metal can be softened when converted into malleable castings, see p. 161.

[2] The relations existing between carbon and iron—and, in fact, between iron and other elements commonly associated with it—is a problem presenting much difficulty. The generalisation given above—combined and free carbon—only expresses part of the truth. When white cast irons, free from manganese and sulphur, are heated for a prolonged period, at a high temperature, but below fusion, the characteristic brittleness is lost, and the metal becomes more or less malleable (see "Black heart" Castings). It would appear—since no appreciable diminution in the amount of carbon present takes place—that the carbon contained in the metal separates from it and remains distributed in a finely divided state throughout the mass, *free* but not *crystalline*.

Further, the carbon in hardened steel differs from that in the annealed or unhardened metal, the two states being known as "hardening" and "carbide" carbon respectively. Probably in both the latter cases the carbon is in combination,

Silicon occurs in pig iron in amounts varying from 0·5 to 12 per cent., being introduced in smelting. The amount present depends on the working conditions of the furnace—temperature, rate of driving, proportion of fuel, etc. It renders cast iron more fusible and fluid, and tends to cause the separation of carbon as graphite, thus rendering the metal softer and tougher. In irons containing little carbon it has a hardening effect, and increases the tenacity. It lowers the melting-point, and its presence in mild steel favours the production of sound ingots.

Iron and steel containing 4 per cent. of silicon is employed for electro-magnetic purposes on account of its low hysteresis properties.

Manganese.—This metal is reduced in the blast furnace. Some pig irons made for special purposes—ferro-manganese—contain up to 85 per cent. of metallic manganese. Pig irons containing more than 7 and less than 30 per cent. are known as "Spiegeleisen" (German = "mirror-iron"), so called from the bright crystalline fracture. With larger percentages the structure becomes more granular. Ordinary pig iron contains from 0·0 to about 2·5 per cent. Its effect is to whiten the iron by retarding the separation of graphite. Manganese lowers the melting-point, and cast iron containing it does not pass through a pasty state before fusion.

Manganese is looked upon as the principal physician of the steel maker. Iron, free or nearly free from carbon, which has been exposed to an oxidising atmosphere in a fused state at a high temperature, loses its toughness and malleability. It has the properties of **burnt iron.** This is probably due to the formation of a suboxide of iron, which is diffused through the mass. Manganese has a greater affinity for oxygen than has iron, and, on its addition, reduces the oxide, forms manganous oxide, and passes into the slag. The iron regains its malleability. The addition made for this purpose always slightly exceeds that required to remove the oxygen, the excess necessary depending on circumstances, notably on the amount of sulphur present. It decomposes the iron sulphide, which, being soluble, is diffused in the iron and seriously impairs the malleability, welding, and other working properties. The sulphide of manganese which forms is insoluble in iron and segregates. This may be partly removed if time to rise to the surface be allowed, or form inclusions in the mass. See Fig. 59. Manganese is consequently found in all mild steels made by the Siemens, Bessemer, and other direct processes.

Irons containing much manganese lose their magnetic property.

and both exist in white iron. There are, therefore, *four* conditions in which carbon exists in iron.

Free—(*a*) graphitic, in grey cast iron; (*b*) free but not flaky, in annealed castings.

Combined { hardened carbon, in hard steel } in white pig iron.
Combined { as carbide Fe_3C in annealed steel }

When iron is dissolved in hydrochloric or sulphuric acid, the combined carbon passes off in combination with the hydrogen as foul-smelling compounds, soluble in alkali. Graphitic carbon remains as insoluble. Combined carbon dissolves in nitric acid, giving a brown solution, the depth of colour imparted depending on the amount present (Eggertz Colour Test).

Sulphur is the greatest enemy of the iron and steel maker, on account of its pernicious effects and the difficulty of removal. It combines chemically with iron, forming several well-defined sulphides. Ferrous sulphide (FeS), used for preparing sulphuretted hydrogen, and iron pyrites (FeS_2), are the best known. The former is formed when iron and sulphur are heated together. Its presence in malleable iron and steel induces red shortness—that is, the metal cannot be worked at or above red heat, but cracks under the hammer. It renders iron more difficult to weld, and hence the necessity of clean fuel, free from sulphur, for smithy purposes.

FIG. 59.—Sulphide (round) and Slag (angular) inclusions in bad mild steel. ×120.

The removal of sulphur in purifying pig iron is difficult, and requires that the slag shall be highly basic, and *the fluxes used free from sulphur*. In pig iron its effect is to retard the decomposition of the carbide and whiten the iron, making it harder. Up to 0·2 per cent. it is not objectionable in foundry irons, for castings which do not require fitting and turning, such as columns, etc. Such irons, however, cast indifferently, as they flow sluggishly, and contract to a greater extent on solidifying.[1]

Pig iron used for " Raumur " malleable castings contains sometimes as much as 0·4 per cent. sulphur. See page 160.

Phosphorus.—This element combines with iron with great readiness, forming phosphides. It is reduced from the phosphates in the charge, in the blast furnace, and taken up by the iron. It renders the metal more fusible and more fluid when molten. Irons containing it are employed in making fine light ornamental castings. The metal is weaker and more brittle. In ordinary pig iron it is present from 0·0 to 1·7 per cent., depending on the nature of the ore and the fluxes used. Practically all the phosphorus in the charge passes into the metal, unless the slags are very highly basic, and contain a large proportion of oxide of iron, as in the processes for making malleable iron direct from the ore. Its effect on malleable iron and steel is to increase the hardness more rapidly than does carbon. This hardness is not affected by heating and cooling, as is the case with that element. Steel and iron containing it are cold short, and brittle, although they work well when heated. Mild steel should not contain more than 0·08 per cent. The presence of 0·2 to 0·3 per cent. in malleable iron may not sensibly diminish its tenacity or working properties, as much of it exists in the slag retained by the metal.

[1] Sulphur in iron greatly increases its tendency to corrosion.

Nickel is alloyed with iron in nickel steel for the purpose of raising its elastic limit without diminishing its toughness. Its effects in all cases are very greatly influenced by the heat treatment it receives, and it is imperative that great care should be taken. The amount used varies from 1·5 to 5 per cent. It has a marked effect on the magnetic properties.[1]

In addition to chromium modern rustless and corrosion resisting steels contain from 7 to 12 per cent. Such steels are workable in sheet form.

Chromium up to 1·5 per cent. increases the hardness, tenacity, and ductility without diminishing the toughness. Even in small quantities it produces considerable differences. Steels contain from 0·5 to 1·0 per cent. for general engineering purposes, up to 4·5 per cent. for rapid cutting steels, and up to 18 per cent. in rustless iron and steel. The former is practically carbonless. Ferro-chrome is an alloy of iron and chromium used for introducing it into steel. Pure chromium is also available for the same purpose. The element is also introduced by direct reduction by silicon from chrome iron ore (see p. 41).

Modern **"Free cutting" Steels** for use in automatic and other tools for rapid production methods *contain up to 0·3 per cent. sulphur and 0·1 phosphorus.* The toughness and other properties of the steel are reduced. The cutting effort required is less and tools in consequence of the reduced wear retain their form and dimensions over a longer period. The phosphorus contents were formerly higher.

Tungsten hardens iron and diminishes its malleability. The original Mushet's steel was an alloy containing from 8 to 9 per cent. of tungsten. The new Mushet contains chromium and other metals in addition. Rapid-cutting steels contain up to 18 per cent. Such steels do not require quenching, but are self-hardening—that is, cannot be annealed and rendered soft by prolonged heating. It is brittle, almost silvery white in colour, and very fine grained. Molybdenum is being introduced for the same purpose. Tungsten is also used in many steels for making permanent magnets.

Molybdenum is added to steels in amounts ranging up to 2 per cent. In addition to its hardening effect it reduces brittleness and increases resistance to shock, making the steel more reliable. It is being preferred to vanadium for this purpose.

Vanadium is introduced to increase the toughness and elasticity. In rapid-cutting steels it aids in the hardening process. From 0·3 to 1·0 per cent. may be present.

Aluminium.—Small additions of this metal are made for the purpose of producing sound ingots and castings. It is also added to cast iron for foundry purposes, producing fine-grained and sound castings.

Tin renders iron cold and red short, and unweldable.

Copper.—In modern practice copper is being added to cast steel, malleable iron and ordinary cast iron. It aids in resisting corrosion. Copper steels are capable of age hardening. They are fatigue-resisting and are more readily annealed. In cast iron it has a graphitising effect. The solubility is about 0·6 per cent.

[1] Nomag is a non-magnetic cast-iron alloy containing nickel and manganese and other elements.

Cobalt—4–5 per cent.—is added to steel to increase the life of high-speed steels by raising the red hardness of the metal and maintaining its cutting edge. The ductility is only slightly affected. Its magnetic effect is very great. It raises the magnetic saturation and thus increases the strength of magnets. Permanent magnets for special purposes contain 35 per cent. of the metal.

Manganese may exist in manganese steel up to 13 per cent. Its purpose is to produce a tough hard metal capable of being rolled and worked, with a high tensile strength and elastic limit and extreme resistance to wear for rail points and crossings, jaws of crushes and similar purposes. It is non-magnetic. It is hardened by slow cooling and softened—for working purposes—by heating and quenching.

Nitrogen may occur in ordinary steel in amounts varying from 0·002 to 0·018 per cent. Nitrided steel is surface-hardened by absorption of nitrogen when heated in ammonia gas.

Oxygen.—Most forms of mild steel contain traces of oxygen as oxide, the presence of which influences the casting behaviour of steel and the subsequent working and properties of the metal. Minute quantities less than 0·02 per cent. have sensible effects.[1]

Oxides of Iron.—Three oxides of metallurgical importance are known. **Ferrous oxide** (FeO), **ferric oxide** (Fe_2O_3), and **magnetic oxide of iron** (Fe_3O_4).

Ferrous Oxide (FeO) is not known in the free state. In combination it forms salts as ferrous sulphate (copperas, or green vitriol) and carbonate of iron. It has a great affinity for silica, with which it combines to form fusible silicates. Ferrous monosilicate ($2FeO.SiO_2$) is the principal constituent of many slags produced in refining iron, and in copper and lead smelting. When slags consisting of silicate of iron are heated with carbon, as in the blast furnace, a large proportion of the iron is reduced to the metallic state. The resulting metal is known as " cinder " pig.

Ferric Oxide (Fe_2O_3) is the red oxide of iron. It occurs in a hydrated form (with water) as iron rust, and naturally as various ores of iron. It forms in combination with acids the ferric salts. It has little affinity for silica. If ferrous silicate is roasted in an oxidising atmosphere, the FeO is largely converted into Fe_2O_3, which separates out. When Fe_2O_3 is strongly heated it gives up oxygen, and is converted into Fe_2O_4. It is reduced to the metallic state by carbon, carbon monoxide, hydrogen, and cyanogen, and oxidises both silicon and manganese.

Magnetic Oxide of Iron (Fe_3O_4) occurs native as *magnetite*. It is the principal constituent of the scale which forms on red-hot iron when exposed to the air, or when steam is passed over red-hot iron. It is attracted by a magnet. It fuses at almost white heat, and on solidifying forms a bluish-black, crystalline, lustrous mass, and is present to a large extent in " best tap cinder," the slag from furnaces for reheating iron. Its oxidising power is less than ferric oxide.

[1] Mild steel before the addition of manganese in smelting may contain over 0·1 per cent. of oxygen; after the addition it seldom contains more than 0·02.

It is unaffected by exposure, and a layer consequently protects iron from rusting, if the coating is dense and continuous. Iron is, however, electro-positive to it, and if the coating is imperfect, and the iron is exposed, in the presence of moisture an electrical action is set up which results in the rapid corrosion of the metal.

Barff's Process for protecting iron articles from rust, consists of coating articles with a film of magnetic oxide by bringing them, at a full red heat, into contact with superheated steam. A firmly adherent, dense, but thin coating is thus formed.

Bower's Process.—In this process the coating is formed by heating the articles in a gas furnace, the atmosphere of which is made alternately oxidising and reducing, by regulating the air-supply. The oxidation produces a thicker but more porous coating, the outer layers of which contain Fe_2O_3. This is afterwards reduced to Fe_3O_4, and the coating consolidated and rendered more adherent by the reduction at the high temperature which prevails.

Coslettizing is a method of protecting iron by producing a film of phosphate of iron on the surface.

Ores of Iron.—The principal ores of iron are magnetite, red and brown hematites, specular iron ore, spathose, clay ironstone, and black-band ore.

Magnetite (Fe_3O_4) consists of iron and oxygen. When pure, it contains 72·4 per cent. of metal. It is black or steel-grey in colour, and often crystalline or granular. It gives a black mark on unglazed porcelain (streak), is readily attracted by a magnet, and often magnetised. It constitutes the "lodestone."[1] Its specific gravity is 5·1, and its crystals regular octahedra. It occurs abundantly in Norway, Sweden, United States, Canada, Siberia, etc., in mass

Magnetic or titaniferous iron sand consists of grains of magnetite with a small quantity of oxide of titanum, derived from the weathering of certain felspathic rocks in which it occurs largely. The lighter matters have been washed away, and the heavy magnetite, with the titanic oxide and other heavy matters present, has accumulated. Deposits occur on the shores of Labrador, New Zealand, West Indies, Bay of Naples, etc.

Red Hematite, so called on account of its red colour and streak, consists of ferric oxide (Fe_2O_3), and contains, when pure, 70 per cent. of iron. It occurs both in dense and earthy forms. Kidney iron ore is a dense variety which occurs in masses with a rounded exterior. The specific gravity is 5. It is usually very pure, containing only silica (quartz) as impurity. The more earthy forms of the ore are less pure. The soft varieties are used for fettling puddling furnaces under the name of "puddlers' mine." It occurs in Cumberland, Lancashire (Ulverston), Forest of Dean, Glamorganshire, and Staffordshire, etc., Canada, United States, Spain and Algeria, Saxony, Bohemia, and the Hartz mountains.

Specular Iron Ore is crystallised ferric oxide, and has the same

[1] Anglo-Saxon *laedan*, "to lead."

composition as red hematite. It has a steely-grey colour often darker on the surface, and iridescent. The crystals are modified rhombohedra, often, as in the black incrustations on hematite, thin plates. The streak is red, and the specific gravity 5·2. "Micaceous iron ore," and "iron glance," are names given to a variety with a grey metallic lustre which readily separates into thin plates or scales. Some varieties are ground up for paint, on account of their high density. This ore occurs in Devonshire, Elba (the mine has been worked for 2,000 years), Russia, Spain, Nova Scotia, and elsewhere.

Brown Hematite.—Brown iron ore—Limonite—includes a series of substances consisting of *hydrated* ferric oxide—ferric oxide and water, chemically combined. It contains, when pure, 60 per cent. of iron.

Brown hematite proper is a heavy dense form, sometimes with radiating structure and shining exterior like kidney ore. It is generally very pure. *Gothite* is of an iron-black colour, with crystalline structure. *Wood hematite* resembles wood in being made up of alternate light and dark concentric layers. *Bog-iron ore* is a light, porous, dark-brown mass, often very impure. *Lake ore* is obtained in Sweden and Finland from the bottoms of shallow lakes by dredging with a net. *Umber* is a dark brown, light, earthy body, containing often manganese, copper, and cobalt. *Yellow ochre* is so called from its yellow colour; it is soft, earthy, and unctuous. All varieties give a yellow or brownish streak. The purity of the ores varies greatly. The Forest of Dean ore from the coal measures contains 89 per cent. Fe_2O_3 and 10 per cent. of water, and yields exceptionally pure iron.

The brown hematites of the North of Spain, resulting from the decomposition by atmospheric influences of veins of spathic ore, are very pure, and often contain much manganese. They are imported for making manganiferous pig iron, and for use in steel-making. The Northamptonshire and Lincolnshire ores are a light yellow and earthy, often full of fossil shells from the oolite. Bog-iron ore yields iron only fit for foundry purposes, owing to the large amount of sulphur and phosphorus contained. The moisture present in brown hematites varies from 9 to 14 per cent. In France, Germany, Spain, and Canada, the principal ores smelted are of this nature. Deposits occur in Devon, Glamorgan, Northampton, Lincoln, Cumberland (Alston Moor), and Durham, India, etc.

Spathose (spathic or sparry iron ore), so called on account of its sparry appearance, consists of crystallised ferrous carbonate, $FeCO_3$ (ferrous oxide combined with carbonic acid). When pure it is of an ashen-grey colour, and contains 48 per cent. of iron. The streak is white. It generally contains more or less carbonate of lime, magnesia, and manganese, which crystallise in the same form, and is often more or less decomposed by weathering, with the formation of hydrated ferric oxide, which colours it brown. Some samples contain 50 per cent. of carbonate of manganese, and it was from these ores that manganiferous pig iron was first produced. The manganiferous

brown ores of the North of Spain have been produced by weathering from spathic ore. It occurs in Somerset, Durham, Cornwall, Isle of Man, Styria, Carinthia, Westphalia, Prussia, etc.

Clay Ironstone includes all ores of a compact, earthy, stony character, varying in colour from light grey to brown.

They consist of ferrous carbonate mixed with more or less clayey matter. Sometimes the deposit is nearly pure carbonate of iron, but in an uncrystallised state. The brown colour is due to partial decomposition with the formation of the hydrated oxide (brown hematite). This ore occurs (1) in nodules, sometimes very large, made up of successive layers, in clay ; and (2) in beds, in the coal measures and oolitic strata. The iron present varies from 20 to 37 per cent. The ore is of low specific gravity and of a stony appearance, but on calcining becomes black owing to the formation of Fe_3O_4. Lime, magnesia, and manganese, as carbonates, etc., iron pyrites, galena, zinc blende, and copper pyrites, as also phosphates and sulphates, principally of lime, as well as clay, frequently accompany clay ironstone, rendering the pig iron smelted from it, as a rule, less pure than from other ores. The sulphur in such iron varies, but rarely exceeds 0·2 per cent. in " all-mine pig."[1] The phosphorus ranges from 0·2 up to 1·5. These ores are worked in South Staffordshire, Derby, Notts, Leicestershire, Warwickshire, North and South Wales, Cleveland district in North Yorks, etc.

Their occurrence in conjunction with coal, limestone, and fireclay, furnishing all necessary materials for smelting on the spot, has been one of the principal factors in the development of the British iron trade. Similar formations occur in Belgium and Silesia.

Black-band Ore is a variety of clay ironstone, admixed with more or less coaly matter. This sometimes occurs in layers, giving the ore a banded appearance, hence the name ; it is sometimes present in such large quantity as to colour the ore black, the amount varying up to 30 per cent. These ores occur in North Staffordshire, in Lanarkshire, and in Prussia, etc. They contain from 17 to 30 per cent. of iron. Owing to the bituminous matter present, it is often unnecessary to add fuel in calcining the ore.

Iron Pyrites (FeS_2).—The heavy, yellow, metallic substance so frequently found as " brasses " in coal, occurs extensively. It must be regarded rather as an ore of sulphur than of iron, being used for the manufacture of vitriol. The residue may contain up to 4 per cent. of sulphur. After burning off the sulphur, and after treatment for the extraction of the copper, it is used as fettling for the puddling furnace under the name of " blue billy," or is briquetted and smelted. It consists of ferric oxide (Fe_2O_3).

Processes for the complete removal of sulphur without removal of the copper are now in use. A special method of calcining at higher temperatures is adopted. See Appendix.

[1] A term used to designate iron made from ore without any admixture of cinder from puddling and other processes.

CHAPTER VIII

IRON SMELTING

Introduction.—As already explained (p. 111), when oxides of iron are heated with reducing agents, such as carbon (C), carbon monoxide (CO), hydrogen (H), cyanogen (CN), the oxygen is removed, and metallic iron results. This reaction occurs at all temperatures above redness. Apparently, therefore, the production of malleable iron would be a simple matter, were it not for the facts—first, that the iron itself is so difficult to melt, and second, the infusibility of the associated earthy matters, while, if the temperature be raised, the iron takes up carbon (see p. 106), and at the same time silicon and phosphorus are reduced, and pass into the metal, depriving it of all its malleability and other useful properties.

It follows, therefore, that, to produce malleable iron from ore direct, a low temperature must prevail, the ores must be rich and fairly pure, and the earthy matters fluxed off by some body which will give a readily fusible slag. The only substance available for this is oxide of iron[1] itself. This removes the impurities, mainly silica, as silicate of iron, and by its excess prevents the iron with which it is in contact from taking up carbon. It is obvious that by such methods only the better classes of ore can be treated, and that the reduction is only partial. This method would consequently be very wasteful, while the production would be very limited as to quantity. Methods of this character were formerly the only methods practised. The carbon, silicon, and phosphorus which enter the iron when the reduction is effected at a high temperature can be removed by heating the impure metal—pig iron—in an oxidising atmosphere, or with oxide of iron itself, whereby it is converted into malleable iron.

At the higher temperature employed in making pig iron, other substances, such as lime and magnesia, may take the place of the oxide of iron in fluxing off the impurity, and the reduction is completed. Poorer and less pure ores can thus be treated, and as the length of time which the iron remains in contact with the carbon, etc., during reduction is not limited, the furnaces employed may be of any size compatible with efficiency, and the output thus enormously increased.

This indirect production of malleable iron, by first obtaining pig or cast iron, and purifying it, is found to be more economical under ordinary conditions than the direct processes, and is the one generally followed.

The *ore*, after the necessary preparation, is charged together with the *fuel* (charcoal, coal, or coke, which also serves as the reducing

[1] See Ferrous oxide, p. 44.

agent) and the *flux* into a tall blast furnace, which is kept full, and the materials, as they melt, sink, and make way for fresh additions at the top. The iron is reduced, and by taking up carbon, silicon, etc., becomes fusible at the furnace temperature, and, melting down, accumulates at the bottom. It is removed from time to time by making an opening into the furnace, and allowing it to run out. This "tap-hole" is at other times kept stopped with a mixture of clay and sand. The slag, after reaching a certain height, flows continuously from the furnace, or a separate tap-hole opened only at intervals may be provided for its removal. It is disposed of in various ways (see p. 143).

Preparation of Iron Ores.—The objects aimed at are (1) to remove extraneous matters completely; (2) to break down the ore to pieces of such size that the reduction shall be complete before it reaches that part of the furnace in which the charge is melted down, otherwise oxide of iron would pass into the slag. (3) In the case of spathic ores and clay ironstones, it is desirable to convert the protoxide of iron present into peroxide, to prevent the passage of the iron into the slag, by its combination with the silica in the charge, at a red heat before reduction has been effected.

Washing.—Clay, sand, and similar admixed and adherent matters are removed from heavy ores by washing on iron grids under a stream of water, and stirring the ore about with rakes.

Magnetic Concentration is now followed for the concentration of impure magnetic ores and iron sands. The finely divided material is made into briquettes for smelting or is "sintered."

Calcination.—This is by far the most important process to which iron ores are subject prior to introduction into the furnace. It consists of heating the ore with free access of air.

In this country, only clay ironstones and spathic ores are generally calcined; hematites and magnetites are smelted without this treatment. As they already consist of peroxides of iron, and would lose nothing but some 6 to 12 per cent. of water, which is expelled in the upper part of the furnace, little advantage is derived, and fuel consumed for this purpose would be practically wasted.

In Sweden, however, where these ores are often washed, and where, owing to the lower temperature of blast employed in furnaces using charcoal, all the gas collected from the furnace is not required to heat the air, these ores are also calcined, the waste gases being employed for this purpose.

The operation is conducted in open heaps or in kilns of special construction, in which less fuel is necessary and the air supply and temperature can be better regulated.

Calcination in Heaps.—The ore is piled up on a thin layer of coal, the large blocks at the bottom and the smaller stuff above, and covered with the smaller ore. In calcining clay ironstone, some 10 or 12 per cent. of small coal is mixed with the ore; but with blackband ores this is unnecessary, the burning off of the bituminous matter present furnishing the necessary heat. The heaps are about 5 feet

high, and the sides slope at about 60°, and are partly covered with small ore. They are ignited at one end, at the base, and allowed to gradually burn through, small refuse being used to check the combustion at any point where it is progressing too rapidly.

Calcining in heaps is wasteful in fuel and heat, and the product is not uniformly calcined. Some parts of the heap will be almost fused, and in black-band ores partly reduced, while others are not calcined through, and require a second treatment.

To overcome these difficulties, kilns of some kind are now generally adopted for all but black-band ores, fired either with solid fuel or waste gas.

Calcining kilns are open-topped, circular, or rectangular structures of masonry, or boiler-plate lined with fire-bricks, with openings near the base for admitting air and withdrawing the material. They are charged from above, and generally work continuously.

Rectangular kilns of masonry, with sloping sides, and lined with fire-brick, are employed for calcining in South Wales.

Gjer's calciner, in use in the Cleveland district, is shown in Fig. 60. It consists externally of boiler-plate, and is lined with fire-brick. It is supported by a cast-iron ring resting on short pillars. The descending ore is diverted outwards by the cast-iron cone which projects upward into the kiln. It is charged from the top, the coal and ore being brought in trucks on rails. The ore, on removal, is despatched to the furnace.

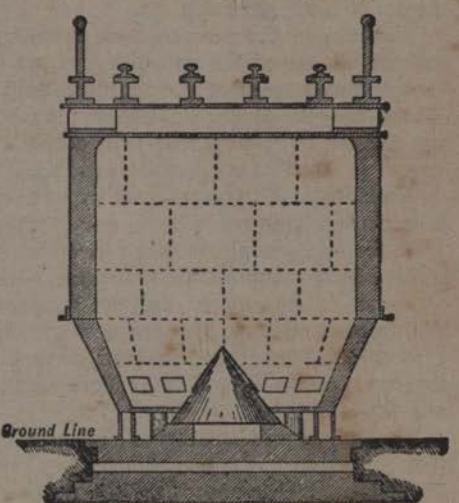


FIG. 60.—Gjer's calciner.

Fillafer's kilns, used in Styria and Carinthia, for the treatment of spathic ores, are narrow rectangular chambers 9 feet high, 4 feet 8 inches long, and 2 feet wide, with fire-bars at the bottom, and a space beneath. Waste gases from the blast furnace are admitted from flues in the side walls near the bottom, and burn in air drawn through the grate-bars. The roasted ore is discharged by withdrawing one or more bars, and allowing it to fall into the space below.

Sintering processes are now being introduced for the agglomeration of small ores and to reduce the sulphur contents. The ore is fed on a grate in a shallow box, an air blast being supplied from below. Fuel is mixed with the ore to partially reduce it and secure clinkering.

Oil burners are sometimes employed. The boxes are so mounted that they can be turned over to discharge their contents.[1]

In calcining, water and carbonic acid gas are driven off, and some of the sulphur in the pyrites present burns to sulphur dioxide and is removed. The bituminous matter in black-band ore is also burnt off. This leaves the ore in an open, fissured, porous condition, in which it is readily acted on in the furnace. The peroxidation of the iron has already been noted. Certain pyritous ores before and after calcining are exposed to the air, or **weathered,** for long periods. The sulphides of iron and copper in the ore are converted into sulphates. These are washed out by the rain or by drenching the heap with water. By this means much sulphur is got rid of, and a purer iron results on smelting. Weathering also facilitates the detachment of pieces of adherent rock.

The *size* of the pieces of ore introduced into the furnace depends on the nature of the ore, the fuel, and the rate of reduction. The slower the descent of the material, and the more open the character of the ore, the larger the pieces may be. Magnetites and hematites are broken in from 1 to 2-inch cubes. The others may be in larger pieces. Stone or ore breakers are used for this purpose.

The Blast Furnace used in iron smelting has undergone great structural changes. The massive masonry structures, braced with iron, formerly employed have given way to the lighter type of furnace known as the cupola blast furnace, and whereas formerly the top of the furnace was open, and the gases were allowed to escape freely and burn at the top, they are now usually closed, and the gases, which resemble producer gas in composition, are collected and conducted by iron pipes to the ground, where they are burnt for heating the blast and for raising steam.

The *height* and *capacity* of furnaces have also greatly increased, so that a "make" of 2,000 tons of pig iron per week per furnace is not infrequent. This amount is often exceeded.

A furnace of an older type is shown in Fig. 61. It will be observed that it consists externally of a boiler-plate casing lined with refractory material, the upper part being supported on columns. The furnace increases in diameter from the *throat* downwards until a maximum diameter is attained at the *bosches*, and then contracts more rapidly, until at a point somewhat above the tuyère openings it becomes nearly cylindrical, a form which it preserves to the bottom. This form, which is the result of gradual development, has the following advantages :—The gradual increase in diameter in passing downward facilitates the movement of the materials as they descend, and by the increased volume detains the ore for a proportionately longer period in this part of the furnace, until certain reactions are completed. In the lower part of the furnace, the rapidity with which the fuel is being consumed, and the materials fused up, with the consequent great contraction in bulk, necessitate the rapid narrowing of the furnace chamber, in order that the charge shall descend to the hearth

[1] See Appendix.

with regularity. The exact internal form, notably the height of the bosches, and the diameter at this point as compared with the height of the furnace, depend on the nature of the ore and fuel, and on the class of iron produced in the furnace.

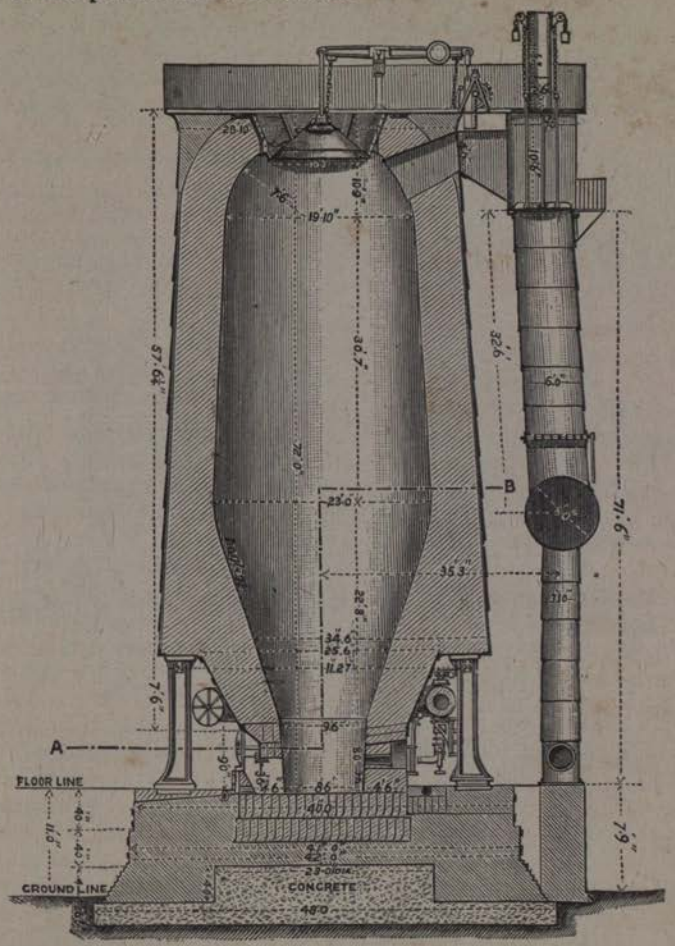


FIG. 61.

The casing of the furnace is made of $\frac{3}{8}$ to $\frac{3}{4}$ inch boiler-plate, well riveted together, and the lining is constructed of 5-inch fire-brick blocks, chisel dressed on both faces and joints, so as to ensure perfect setting and uniformity in the outline of the furnace. These may only form some 18 inches of the lining, and be backed with ordinary fire-bricks, or the whole thickness (3 feet 6 inches to 5 feet) of lining may be thus made.

The upper part of the structure is carried on columns, which rest on a stone kerb bound with iron bands, enclosing the hearth of fire-brick blocks. This stone foundation rests on a bed of concrete. On the top of the columns rests a cast iron ring, some 5 inches thick, cast in segments, and on this the superstructure is built.

A *gallery* or *platform* surrounds the throat of the furnace. This is covered with iron plates, and slopes slightly towards the edge of the cup, which stands some 3 or 4 inches above it, and acts as a stop for the barrows.

The lower part of the furnace is supported by plating attached to the pillars or by iron bands.

From the tuyères downwards the hearth is supported by iron bands and in various other ways.

The throat of the furnace in Fig. 61 is closed by a **bell-and-cone** arrangement. A truncated hollow iron cone cast in pieces and bolted

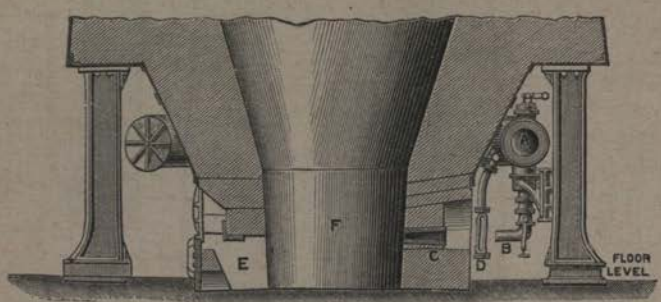


FIG. 62.—Lower part of furnace. A, blast-main (horseshoe); C, tuyère; E, fore hearth; F, crucible.

together, supported in the throat of the furnace, and resting on the masonry by a broad flange, forms the "bell"—the opening into the furnace being closed by the "cone" supported from one end of a lever projecting over the top. At the other end is a counterpoising weight (slightly heavier than the cone), and the apparatus for controlling its motion, when it is lowered to allow of the descent of the material (previously charged into the bell) into the furnace.

Fig. 62 shows an enlarged view of the lower part of the furnace. The blast is brought to the blast-main A, which is an iron pipe, lined internally with fire-brick, if hot blast is employed, supported at a height of about 7 to 8 feet. It encircles the furnace except in front, and from this at regular intervals the blast is conveyed to the tuyères by vertical iron pipes passing downwards, each of which is provided with a throttle-valve to regulate the air-supply. Suspended from these by hangers are the "goose-necks" B, which articulate with the vertical mains by ball-and-socket joints. At the bend of B a mica plate is inserted, known as the "furnace eye," and through it the working of the furnace may be inspected. A sheet-iron blow-pipe

which slides telescopically on B, conveys the blast through the tuyère-block C, into the furnace. These tuyères enter the furnace through small arched or round openings known as tuyère houses, and are closely luted. They generally project a little beyond the front line of the furnace, and are cooled by the circulation of cold water supplied from the water main which surrounds the furnace. When, as occasionally happens, the nose of a tuyère is burnt off, it is removed, and a new one inserted, blast being stopped for the time being. The tuyères in the newer furnaces are of copper and the tuyère opening is supported by a water-cooled block—the jumbo.

The use of water-tuyères became necessary with the introduction of hot blast, on account of the increase in temperature in this region. With cold blast, the absorption of heat by the expansion of the cold air so cooled the furnace just in front of the tuyères, that the slag solidified on the end, and formed a prolongation or slag nose, from the length of which the working could be judged.

Fig. 63 is the **Staffordshire tuyère.** It is a conical water jacket encircling the blow-pipe, cooled by water circulating between the casings.

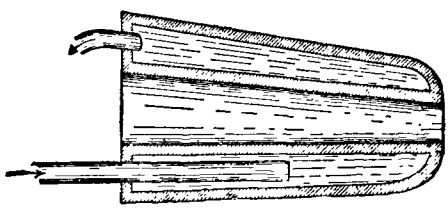


FIG. 63.

In the **Scotch tuyère,** the water circulates round a coil of wrought iron pipe embedded in a cast-iron block.

The **Spray tuyère** is a hollow casing, and the water is sprayed on the front through holes in the pipe conveying it.

The modern copper tuyère and jumbo are shown in Fig. 64.

The *size* of tuyère is proportioned according to the volume of air and the pressure employed, so that the blast is carried well into the furnace, and does not creep up the sides. The blow-pipes from the goose-necks fit tightly into the tuyère, and are luted round with clay, to prevent escape of air.

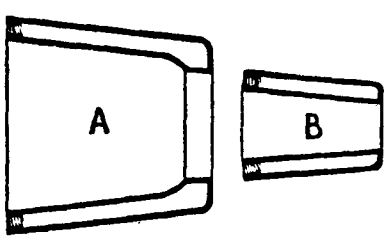


FIG. 64.—Copper tuyère (B) and jumbo (A).

Modern Blast Furnace.—Figs. 65 to 73 show the nature of the improvements made in the construction of modern blast furnaces rendered necessary by the increased rate of driving. The furnace shown in Fig. 61 made approximately 600 tons of pig iron per week. A modern furnace may make 1000 to 3000 tons, or much more, in the same time. Greater facilities for the disposal of products and handling the larger amount of raw material and for dealing with the altered conditions arising from the enormous increase in the amount of heat necessary to smelt the augmented charge

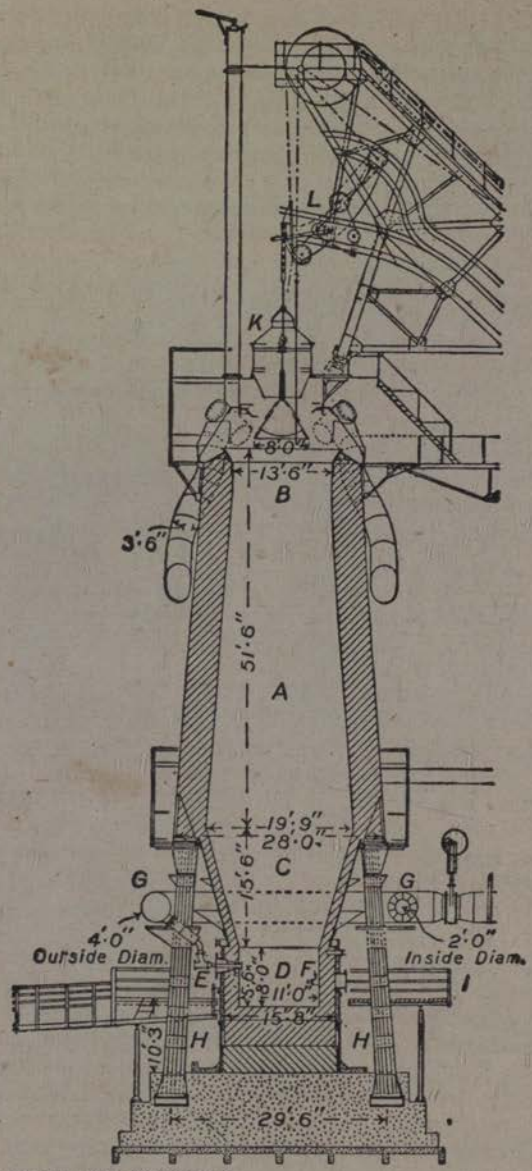


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FIG. 65.—Vertical section of modern blast furnace. A, stack; B, throat; C, bosches; D, hearth; E, blast main blowpipe and tuyère; F, slag notch; G, horseshoe main; H, supporting columns for stack; I, platform; K, charging bucket; L, carriage.

are obviously required. The main modifications are concerned with (*a*) the cooling of the walls and bosches to preserve the refractory lining; (*b*) the capacity and better support of the hearth; (*c*) the supply and distribution of the blast; (*d*) the disposal of slag; (*e*) the collection of the gases; and (*f*) the charging apparatus.

Fig. 65 shows a section of a modern furnace. The hearth D is supported by steel armour and is not embedded. The brickwork of the bosches C is only 18 inches thick and is cooled by water flowing down the iron plates from the cascade arrangement shown. Four

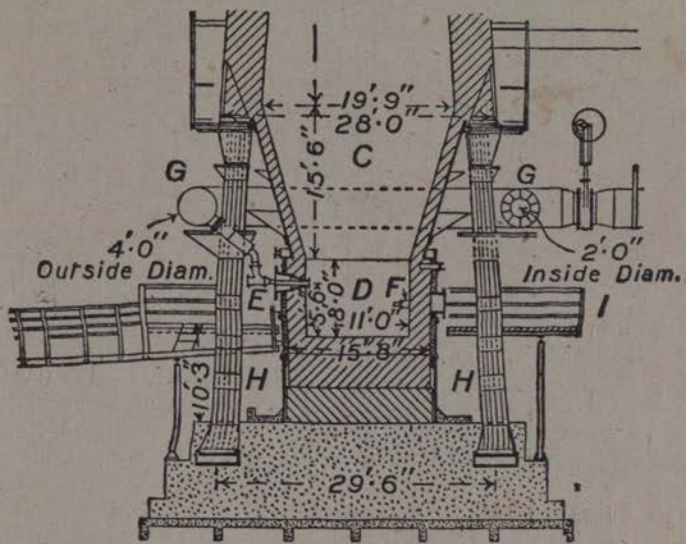

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FIG. 66.—Lower part of furnace shown in Fig. 65. C, cascade cooled bosches; D, hearth; E, blast mains and blowpipe entering tuyères; F, water cooled slag notch; G, horseshoe main; H, columns supporting stack; I, platform.

3 feet 6-inch pipes symmetrically disposed are provided to remove the furnace gases. By this means the distribution of the ascending gases is kept uniform. The charging apparatus is a bell and cone, but the charge is conveyed to the top of the furnaces in special buckets K which fit closely on the top of the bell. The buckets are slung from the carriage L, running on the inclined skipway, and on reaching the top the carriage tilts, deposits the bucket on the charging bell, lowers a cover on the top of the bucket, and depresses the charging cone in succession, the changes taking place in the reverse order when the carriage is hauled back.

The **hearth, or crucible,** of the furnace, in which the iron collects, is shown in Fig. 66.

A fire-brick lining 27 to 32 inches thick is supported by a steel

casing which is often water cooled and is clear of obstruction and accessible all round. Attention to tuyères and other necessary appliances is possible from a platform surrounding the furnace at a convenient height.

The bottom consists of a solid mass of fire-brick from 5 to 12 feet or more in thickness carried on a broad thick concrete foundation.

The *tap-hole* is at the bottom. It is a rectangular opening several inches square, kept closed until the metal has accumulated almost to the level of the slag-notch, by a mixture of clay with sand, or coal-dust. This is broken away by a pointed bar when the furnace is *tapped*, and the metal allowed to flow out. While this is being done the blast is shut off

The slag notch is situated a few inches below the level of the tuyères. In modern furnaces a water-cooled casing is built into the furnace structure and the slag is tapped at regular intervals into slag-ladles on wheels. These are hauled away to the tip and emptied while the slag is in a molten state.

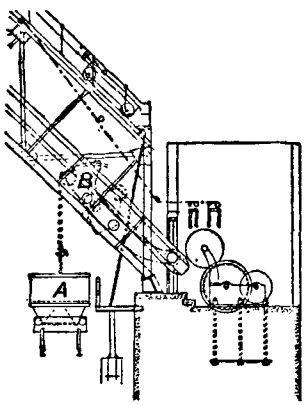

FIG. 67.—Showing charging tub at bottom of incline.

Fig. 67 shows the charging bucket on its bogie at the bottom of the inclined skipway. The bucket A is closed by a cone at the end of the rod by which the bucket is slung.

Fig. 68 shows the enlarged section of the furnace top. The bucket D is in position for charging. A is the charging bell; B the charging cone and C counterpoise weights, of which there are three. When the cone E is depressed it operates B and the charge passes into the furnace. F is the cover to prevent escape of gases, and when E is raised the weights C bring back the charging cone and close the furnace throat.

Fig. 69 represents the lower portion of a modern blast furnace with the bosches cooled by water blocks (Fig. 70) built into the brick-work. It will be noted that the water circulates from tier to tier and that the discharge pipes empty into troughs and are under observation. Fig. 71 shows the lower part of a furnace of recent construction. The bosch is surrounded by a water jacket in the form of a spiral trough—Sahlin bosch. The water cooling of the furnace walls is rendered necessary by the excessive development of heat when the furnace is being rapidly driven, *i.e.* making a large output, more coke having to be burnt to supply the heat necessary to melt the iron and slag, and to supply that lost by radiation and in other ways. See also Figs. 72 and 73.

Owing to the enormous amounts of material required by modern furnaces, the simple bell and cone arrangement shown in Fig. 61

has been replaced by other methods of closing the throat and admitting the charge.

Opening the furnace top too frequently would involve a large loss of gas, and otherwise interfere with the regularity of working. (Each ton of iron smelted from an ore containing 50 per cent. iron requires

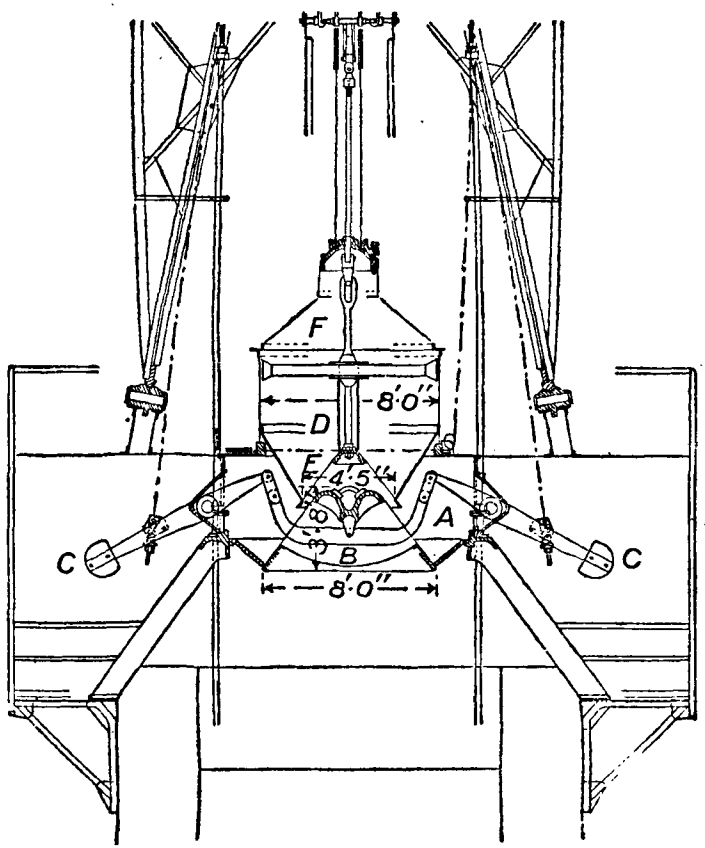

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FIG. 68.—An enlarged view of the top of furnace, Fig. 65.

approximately 3·5 to 4 tons of solid material, made up as follows: ore 2 tons, coke 1 to 1·25 tons, limestone 0·5 to 0·75 ton. For each 1,000 tons per week made, this would mean the introduction of nearly 600 tons of charge per day, or 25 tons per hour.)

Fig. 74 shows a double bell-and-cone arrangement. The material is tipped into the upper bell which is closed after letting down the material to the lower bell. The charging-cone is then lowered.

Fig. 68 shows a charging bucket which fits over the bell and closes

it while its contents are transferred to the charging-bell and afterwards admitted to the furnace.

In other devices (Brown and McKee) a hopper with side delivery is mounted over the bell. In some forms this can be rotated by spur wheel or worm wheel mechanism so as to direct the charge into the

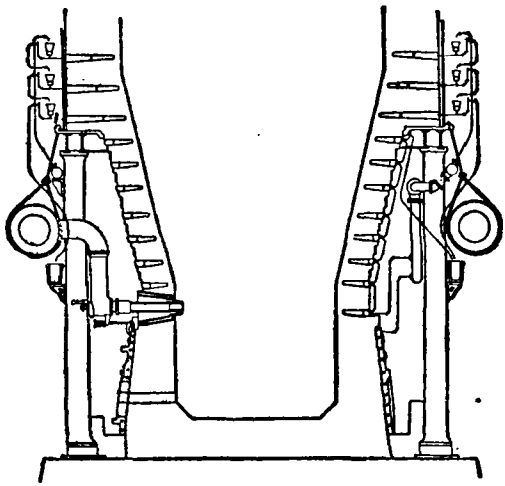


FIG. 69.—Bosches cooled by water blocks.

bell in any position or, while revolving, to secure uniform distribution and loading of the cone. The charge is raised to the top by self-tipping skips on an inclined track.

These methods of closing the throat, when properly designed, give the most regular distribution of materials attainable in mechanical charging, the ore, flux, and fuel falling in an annular heap some distance from the wall and from the centre. The larger stuff consequently has an equal tendency to roll towards the sides and middle, and the inequalities working away as the charge descends into the wider part of the furnace, uniform obstruction is offered to the blast, which in consequence distributes itself regularly, having no tendency to creep up the sides or middle, as would be the case if the large stuff accumulated there.

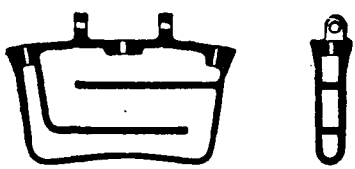
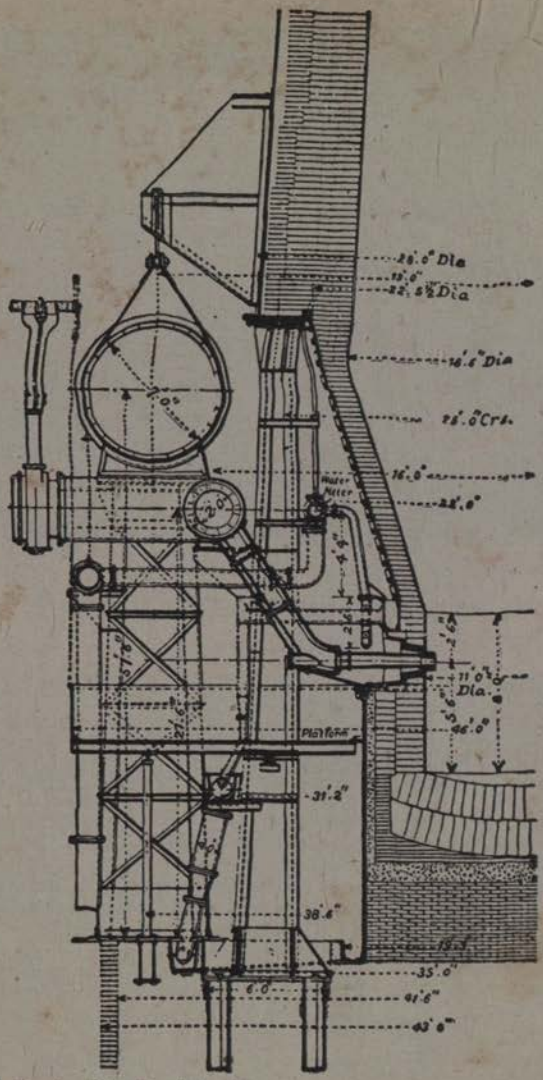


FIG. 70.—Water-cooling block for bosches.

In modern furnaces there is no charging platform. No men are employed at the top, all control of the charging appliances being effected from below.

The height of blast furnaces varies from 60 to 110 feet, and the diameter of the bosches from 17 to 30 feet. The ratio of height to diameter $= \frac{H}{D}$ varies from $3\frac{1}{2}$ to 6. Such a furnace, with a height of



Pearson & Knowles, Ltd., Warrington.]

FIG. 71.—Half section modern blast furnace, showing Sahlin water-cooled bosches.

85 feet, and bosch diameter of 17 feet, has recently been put to work. The height of the columns varies from 10 to 21 feet 6 inches, and the diameter of the hearth from 8 to 11 [1] feet, and its depth from the slag-

[1] This is exceeded in furnaces using blast at high pressures. In some American furnaces a diameter of 21 feet 6 inches has been reached.

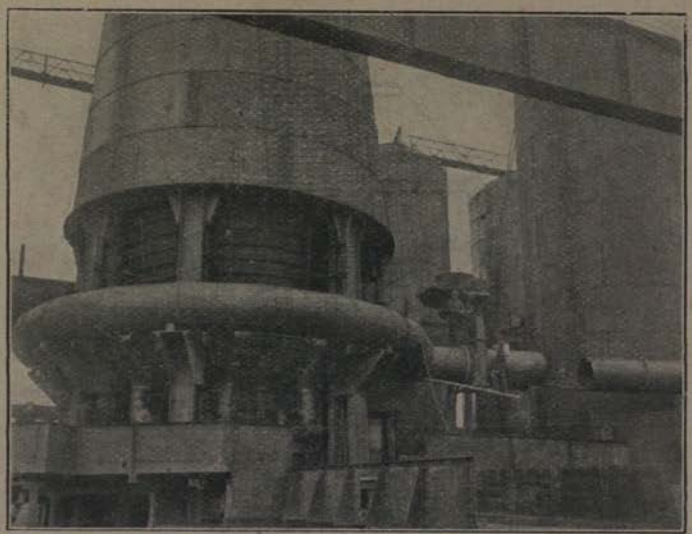


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FIG. 72.—Lower part of modern blast furnace with water-cooled Sahlin bosch

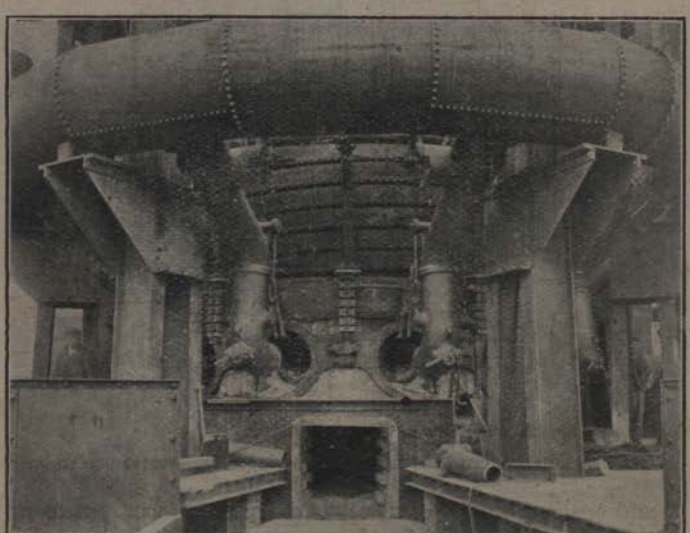

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FIG. 73.—Lower part of modern furnace showing horseshoe and blast mains and connections, water connections, tapping hole, etc., before being blown in.

hole to the bottom is 8 to 10 feet. The number of tuyères ranges from 8 to 16, and they are distributed at equal distances round the hearth. Usually only one row of tuyères is employed, but in some modern furnaces two or even three rows have been introduced in order to supply the amount of air required. The upper tuyères are only useful in special circumstances.

The **gases** pass through the openings at the side into the "downcomer," and are led away to boilers, stoves, etc., where they are burnt. Excess of gas burns at the mouth of the standpipe seen on the right of Fig. 61.

Dust Catchers.—Considerable amounts of finely divided solid material are carried from the furnaces by the escaping gases and chambers and special contrivances through which the gases are led are provided to secure its removal.

The modern practice of rapid driving involving much greater velocity in the gas current has increased the losses from this cause and made the use of dust catchers a necessity.

Lifts.—The charge, consisting of ore, flux, and fuel, is raised to the top by means of vertical lifts, or is drawn up inclined planes.

Inclined skipways so designed as to make the skips discharge their contents into the bell automatically are employed in modern furnaces.

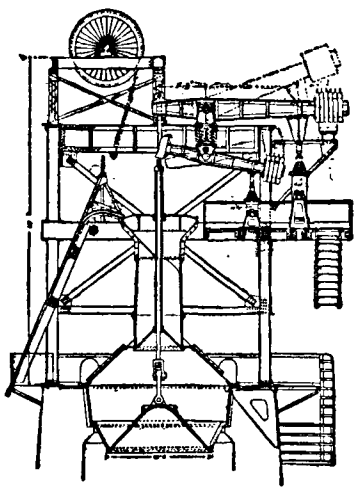


FIG. 74.

The Charge.—The proportions of the materials in the charge must be separately determined for each ore and fuel, and even for each furnace, the fuel consumption being influenced by the volume, temperature, and pressure of the blast, as well as by the nature of the fuel. More coal, for example, must be used than when coke is employed. With clay ironstones containing, after calcination, 35 to 42 per cent. of iron, the charge consists of from 48 to 57 cwts. of ore, 19 to 25 cwts. of coke, and 10 to 14 cwts. of limestone per ton of iron made, the temperature of blast varying from 500° to 700° C., and its pressure from 3½ to 15 lbs. In furnaces using coal,[1] from 2 to 2½ tons replace the coke.[2]

For red hematite the charge consists of 33 to 40 cwts. of ore, containing from 50 to 60 per cent. of iron, 7 to 10 cwts. of limestone, and 19 to 25 cwts. of coke, and, if very siliceous, about 1¼ cwt. of aluminous ore (see Fluxes).

[1] See p. 81.

[2] The coal is coked in the upper part of the furnace.

In smelting magnetites with charcoal, from 16 to 25 cwts. of charcoal are consumed per ton of iron made.

Some ores contain all the ingredients necessary for fluxes, and are described as *self-going* or self-fluxing.

The proportions existing between the ore and fuel in the furnace are described as the **burden**. It is " light " when the fuel is in large proportion, and " heavy " when the quantity of fuel is diminished.

This determines the amount of heat generated, and thus the temperature of the furnace.

With light burdens, speaking generally, more silicon is reduced, more carbon taken up and greyer iron—see p. 140—is produced.

The height of the materials in the furnace is maintained at a constant level—the stock line—fresh additions being made at intervals of from 10 to 20 minutes.

The Blast.—Time was when bellows worked by hand supplied the air necessary for the low furnaces—seldom exceeding 10 feet high—then employed. Some of our large modern furnaces require as much as 50,000 cubic feet of air per minute, at pressures of $3\frac{1}{2}$ to 15 lbs. This is supplied by means of blowing-engines, some of which are capable of delivering as much as 60,000 cubic feet of air per minute. These engines are of various forms. A huge cylinder, sometimes 12 feet in diameter and 12-feet stroke, fitted with a solid piston, is provided with valves in such a manner that, as the piston travels to and fro, air is drawn in at one end and expelled from the other, or, in other words, the cylinder is double acting—filling one end and discharging the other, in whichever way the piston is travelling. These blowing-cylinders are connected with steam or gas engines, by which they are worked. The air is delivered at a pressure varying from a few ounces up to 15 lbs., if desired, determined by the diameter of the furnace, the resistance of the charge, and the nature of the fuel. Turbine blowers are now being largely used. They occupy much less space than ordinary blowing engines for the same amount of air delivered. Low pressures are employed for charcoal furnaces, and the higher in coke and anthracite furnaces. About $2\frac{1}{2}$ to 3 lbs. is employed in furnaces using coal.

Note.—In modern blowing-engines the tendency is to increase the number of blowing-cylinders and diminish their size. In the same furnace, with similar materials, the pressure of the blast influences the quality of the iron produced. Low pressures and large volume, and consequent rapid driving, increase the make but lower the grade of iron. Higher pressures, with less volume and slower driving, diminish the make but improve the quality (see Reactions in Furnace).

Hot Blast.—Formerly the air was supplied to the furnace at the temperature of the atmosphere. In 1828, Neilson, at the Clyde Iron Works, commenced the use of heated air, and in a few years its use became general.

The advantages derived are—

(1) The use of raw coal (of certain classes) instead of coke.

(2) Much less fuel is required in the furnace, owing to the heat carried in by the air.

(3) The temperature in front of the tuyères is increased, and the fusion zone of the furnace brought lower down.

(4) The furnace works with greater regularity, and is more under control, not being affected by atmospheric influences.

Note.—Each ton of carbon burnt to (CO) carbon monoxide requires about 6 tons of air—12 parts of carbon requiring 16 of oxygen. If air contains 23 per cent. by weight of oxygen, then $\frac{16}{23} \times 100 = 69{\cdot}55$, or each part of carbon requires $\frac{69{\cdot}55}{12} = 5{\cdot}8$ (nearly) parts of air. Since only 3·5 to 4 tons of solid material (ore, fuel, and flux) are required to make a ton of iron, and, on an average, each ton of iron requires about a ton of carbon (as coke) for its production, it will be seen that about 6 tons of air, equal to nearly one and a half times the weight of solids, will be required to produce it, and will produce nearly 7 tons of gases, consisting of carbon monoxide and nitrogen, together with small amounts of other gases (see page 103). This air has to be raised to the furnace temperature on entering the furnace, while the solids (including the fuel) have been preheated by the hot gases ascending the furnace. The specific heat of the air is high, higher than the solids, and the amount of heat necessary to raise the temperature to that of the furnace is consequently large. (Average specific heat solids is approximately 0·13 of the air 0·22.) This heat is absorbed at and near the point where the air enters, hence the hottest part of the furnace is slightly above, and not in front of the tuyères, the colder the air and the larger the amount of heat absorbed and the higher the point of maximum temperature.

The heat carried in by "hot" blast diminishes the amount that must be absorbed from the furnace, and thus the amount of fuel required for smelting. If it were possible to raise the temperature of the blast to that of the furnace no heat would be absorbed, and the economy would be increased accordingly. Owing to the difficulties of dealing with air at that temperature this is impossible in practice.

For similar reasons an increase in the proportion of oxygen in the blast and consequent diminution in the nitrogen would reduce the volume of air necessary, and both increase the temperature and lower the "hot" zone. This has been attempted, 2 per cent. of O_2 obtained from liquid air, being added. Economic conditions are unfavourable to the development of the method.

The temperature of blast employed depends on the fuel and class of iron made. With charcoal it is only heated to from 200° to 350° C.; with anthracite and coke, temperatures of from 700° to 800° C. are employed. The higher temperatures tend to produce greyer irons, containing more carbon and silicon.

Blast Stoves.—The air is heated by passing it through cast-iron pipes, or through brickwork regenerators, heated by the burning of the waste gases collected from the top of the furnace.

Fig. 75 shows a cast-iron pipe stove. The air circulates through the pipes in the chamber, from end to end, as shown.

In pipe stoves a temperature of 550° C.[1] (1022° F.) cannot be exceeded without danger of rapid oxidation and fracture of the pipes. The products of combustion escape at a temperature equal to or greater than that to which the air is raised, and carry off at least one-half of the heat generated.

[1] This is seldom realised in practice. From 600° to 900° F. (315° C. to 482° C.) are the usual temperatures.

In regenerative hot-blast stoves, the principle of the Siemens regenerative furnace is embodied. The waste gases collected at the throat of the furnace are burnt in the stove, and the products of combustion drawn through brickwork flues on their way to the stack. The heat is thus absorbed, and by passing the blast through the stove in a direction opposite to that taken by products of combustion, it may attain the temperature of the stove. At least two such stoves working alternately—one being heated up while the other is in use for heating the blast—will be required. In recent installations four stoves are provided for each furnace, often with the addition of an equaliser. The advantages derived from their use are: (1) higher temperature of blast; (2) less loss of heat, resulting in greater fuel economy; and (3) absence of difficulties arising from the burning, cracking, and leakage of iron pipes.

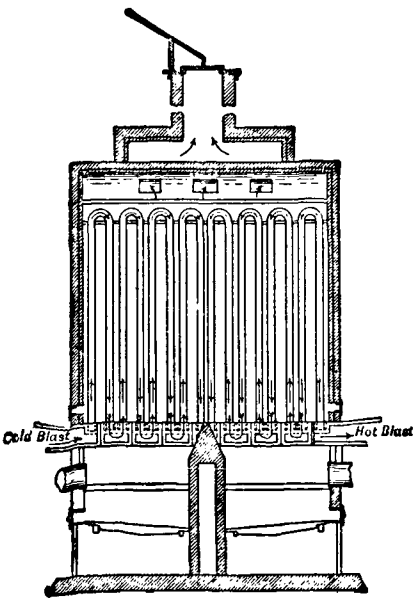


FIG. 75.—Cast-iron pipe stove.

Cowper's Regenerative Hot-blast Stove is shown in Fig. 76.

The waste gases from the furnace are brought by the culvert V, and enter the flame or combustion flue O, through the valve F. Here they are burnt by the admission of a suitable supply of air through G. The products of combustion ascend and are drawn down through the passages in the brickwork P—ordinary chequers, or built of special bricks—in passing through which they are deprived of nearly the whole of their heat. The brickwork gets first heated near the top, but the heating gradually extends downwards. The chequer is carried on cast-iron grids supported by short brick columns. Doors for cleaning-out purposes communicate with the space beneath. In passing through the chequers, the products of combustion are cooled down to about 150° to 200° C., at which temperature they pass into the chimney-flue U, and thence to the stack; the heat thus carried away doing useful work by creating a draught through the stove.

When the stove has been heated to a maximum about halfway down, the supply of gas is stopped, and the air- and chimney-valves closed. The valve of the cold-blast main, through which air passes under the chequer, and the hot-blast main E, which communicates

with the combustion-flue, are opened. The cold air rising through the hot brickwork gradually becomes heated *by contact* with it as it

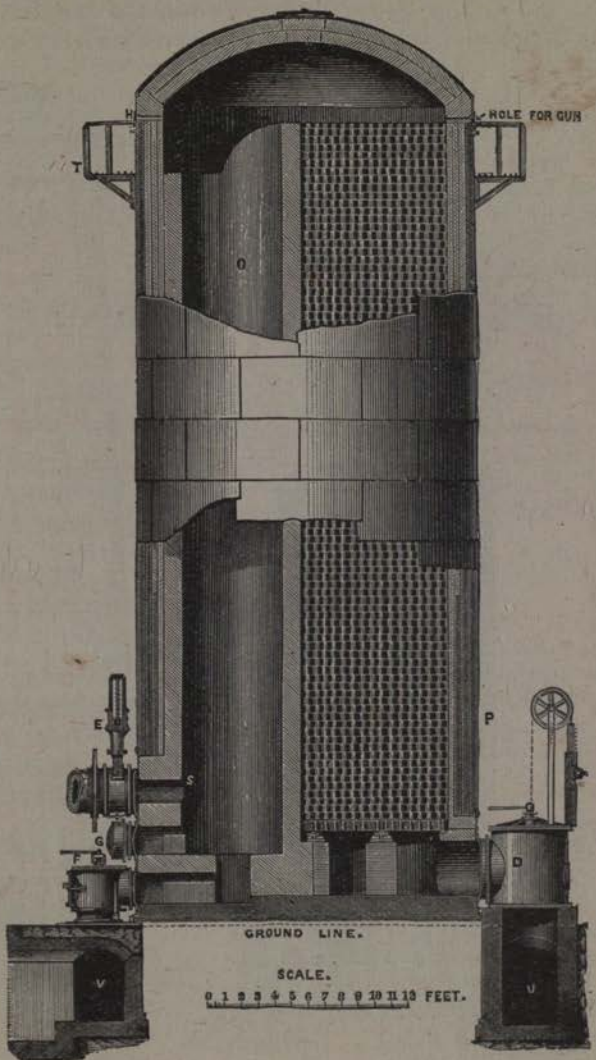


FIG. 76.—Cowper's hot-blast stove.

ascends, until it has attained the temperature of the stove. It then passes through the remaining upper portion without further absorption of heat, and, being collected at the top, passes down the flame-flue into the hot-blast main.

To prevent, as far as possible, dust being carried into the stoves, the waste gases from the furnace are passed through dust-catchers, in which the current of gas is slowed down and the dust in large measure deposited. Dust in the stove reduces its efficiency.

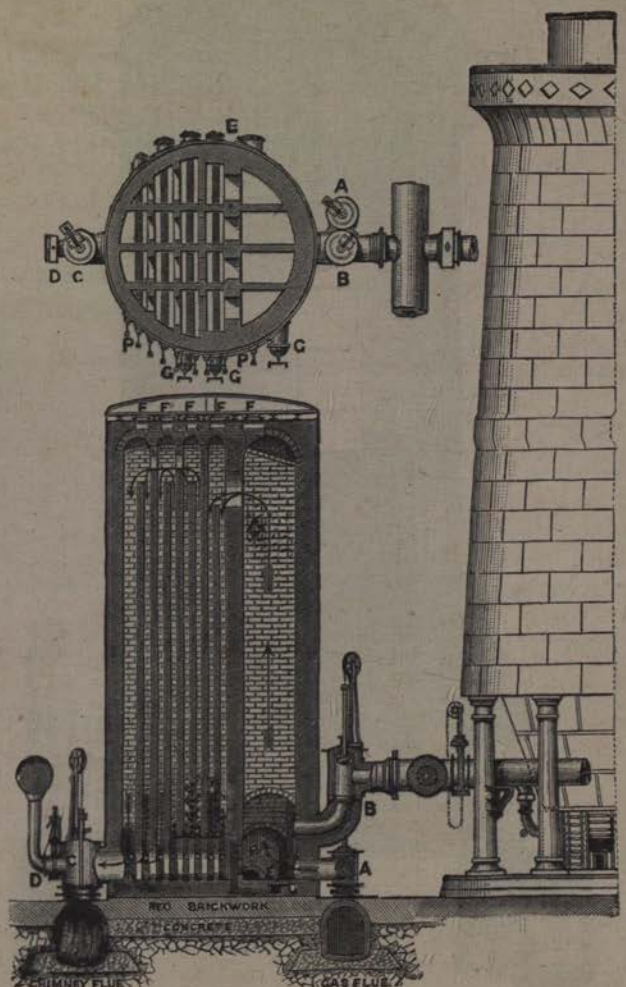


FIG. 77.—Whitwell hot-blast stove. A, gas-valve; B, hot-blast main; C, chimney valve; D, cold-blast main; E, doors for removing dust; F, cleaning holes through which scrapers are introduced; G, air inlet; P, inspection openings.

Whitwell's Stove is shown in Fig. 77. The chequer-work of the Cowper is replaced by vertical walls, to facilitate cleaning.

In regenerative stoves the blast is heated to temperatures varying

from 1200° to 1400° F., and the stoves are changed at intervals of from half an hour to two hours.

The large capacity of modern stoves—a gross volume of 14,000 cubic feet including the chequers being often exceeded—serves to equalise the pressure, but with rapid driving and several stoves in different stages of cooling in use, a temperature equaliser through which air from all stoves passes is often employed. It resembles a stove, but is not heated by gas.

In other types of stoves the combustion chamber may be in the middle of the stove, and/or the chequers may be divided into sections to secure better distribution.

In modern working for ordinary purposes the temperature of blast is maintained as nearly constant as possible between 1100 to 1200° F. at the tuyères. Provision is made in some cases to allow cold air to mix with the blast if too hot in order to keep working conditions uniform.

Pressure gauges and temperature recorders are inserted in the blast main to enable this to be done.

Dry Blast.—All the moisture carried into the furnace by the air blown in, undergoes decomposition with absorption of heat and consequent cooling of the furnace or waste of fuel. Most of the hydrogen in the gases is produced in this way. In many cases the air is now dried prior to entering the furnace.

Three methods are followed :—

(1) Freezing out the moisture.
(2) Desiccation.
(3) Cooling after compression.

The first method depends on the relation between temperature and vapour pressure. The heat removed has to be subsequently restored. In the second the moisture is absorbed by calcium chloride in solution (calcium brine). Dried blast should not contain more than 2 per cent. moisture.

In **blowing in** a furnace, as in heating up any large mass of brickwork, the greatest care has to be exercised. The masonry is first dried by wood fires, and then fuel gradually added until the furnace is half full; a small blast, through, say, a ½-inch nozzle, is then introduced, and a little limestone added to flux off fuel ash. The charging of material may then commence, a much larger proportion of fuel than will ultimately be used being present in the charge. The size of the nozzles is gradually increased until the full volume and pressure of blast have been attained, the time elapsing before this is reached sometimes being as long as 18 days. The ore and flux are also gradually increased until they reach the normal amounts.

In " blowing out " a furnace, the burden is gradually diminished, and at the last only fuel and a little limestone are fed in, so that the furnace is completely cleared.

When an accumulation of material forms at any point in the furnace, which from some cause or other will not work down, the irregularity is described as " scaffolding," or " hanging," of the charge.

The formation of such obstructions is generally due to lack of heat resulting from the failure of the hot gases which carry upward the heat generated by the fuel, to penetrate the material owing to close packing, often the result of fines in the charge. Hence the importance of regular distribution of the charge.

If fines accumulate in the middle of the furnace or the blast fails to penetrate " pillaring " may occur.

In all such cases the temperature of the collected gases is raised and gives indication of the condition of the furnace. Local overheating may occur and "hot spots" be formed.

The sudden descent of the "hanging" material, owing to the melting away of the support, is called a "slip." It is sometimes attended with serious con

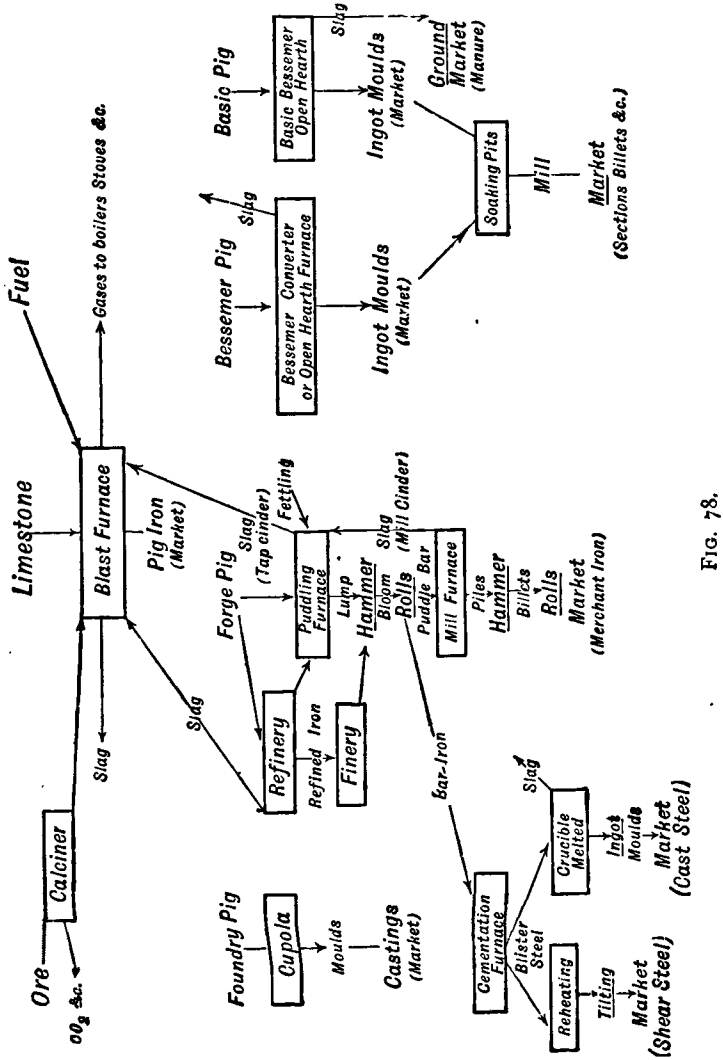


FIG. 78.

sequences. When the "slipping" charge contains cavities, very large amounts of carbon-monoxide may be suddenly brought into the hearth. An explosive mixture may be suddenly formed by carbon monoxide and air with disastrous results. When the blast is off this danger is minimised. "Slipping" is sometimes resorted to to keep the furnace clear. Cutting off the blast reduces the upward air pressure under the charge. With high pressures and in wide furnaces the

supporting value of this is considerable. Its sudden removal may cause the charge to drop to the hearth.

The formation of infusible masses of iron, often containing titanium, in the hearth and lower part of the furnace seldom occurs since the introduction of highly heated blast. They are known as " bears."

The furnace being in full work, the charging of fresh material at the top goes on at regular intervals. The metal accumulates until the hearth is full, and is then tapped out by piercing the clay stopping of the tap-hole with a pointed bar. A channel leads from the front of the furnace to a sand bed which slopes very slightly from the furnace. This main channel is continued, in the sand, to the front of the bed, sending out side channels at intervals, which serve as feeders for long rows of roughly made ⊔-shaped open moulds, lying like huge combs in the sand. The feeders are picturesquely named " sows," and the metal in the moulds " pigs." After filling the first row, the row of moulds furthest from the furnace is next filled, and the others in succession, the metal being prevented from entering the upper rows by stops. When the metal becomes solid, the pigs are detached and the sows broken up into convenient lengths with sledge-hammers. The pigs are about 4 feet long and 4 inches across the surface. Casting machines having iron moulds are also used.

Swedish pig and ferro-manganese are generally cast in wide, open, iron moulds into plates, which are broken up.

In modern furnaces the metal is often tapped into ladles for transfer to metal mixers for use in steel-making furnaces and converters, or it may be transferred to containers for use in the foundry. These containers are sometimes heated. Excess of heat and gases are eliminated as the metal stands but success is dependent on the production of a uniform product by the furnace.

CHAPTER IX

CHEMICAL REACTIONS OF BLAST FURNACES

In considering the chemical changes going on in the furnace, the conditions under which it works must be borne in mind.

The materials charged in at the top occupy a considerable time in descending the furnace, varying from nine hours to two or three days, according to the nature of the material, the quality of the iron being produced, and the quantity of blast; the charge descends most rapidly with the heavy burdens and large blast employed in making white iron. In its descent, the oxide of iron is reduced to the metallic state by the carbon monoxide in the ascending current of hot gases, and the various substances [1] found in pig iron are introduced into the metal. But little consumption of fuel takes place until it arrives in the vicinity of the tuyères. Here the oxygen of the air combining with the carbon produces carbon monoxide (and perhaps a little carbon dioxide, which is at once reduced to monoxide by the excess of carbon present), producing heat for the fusion of the metal and slags.

With hot blast this zone of fusion is immediately above the point at which the blast enters. With cold blast, owing to the absorption of heat by the expansion of the cold air blown in, this part of the furnace is somewhat cooled, and the zone of most rapid combustion extends higher up the furnace.

This gas, together with the nitrogen of the air and any hydrogen resulting from the decomposition of water-vapour in the air blown in, ascends, and is the principal active reducing and carburising agent in the furnace. As the materials in the lower part of the furnace are burnt away and melted up, those above gradually descend, passing through hotter and hotter regions till the fusion zone is reached.

The reactions by which the iron is reduced and carburised are of a somewhat complicated nature, depending on the relative affinities of carbon and iron for oxygen, at varying temperatures.

The only change taking place in the upper part is the gradual heating up of the charge. When a sufficiently high temperature has been attained, the reduction of the iron commences. The carbon monoxide, CO, combines with the oxygen in the oxide of iron, forming carbon dioxide, CO_2, and liberating the iron—

$$Fe_3O_4 + 4CO = 3Fe + 4CO_2$$

This action commences at temperatures considerably below a red heat, and the oxide is gradually reduced to a spongy mass of metallic iron, which includes all the gangue in the ore.

[1] Carbon, silicon, manganese, phosphorus, and sulphur.

At temperatures a little below, and above redness, spongy iron decomposes carbon monoxide, carbon being separated and oxide of iron formed, which is subsequently reduced by carbon—

$$3Fe + 4CO = Fe_3O_4 + 4C$$
$$Fe_3O_4 + 2C = 3Fe + 2CO_2$$

These reducing and carburising actions go on side by side.

The spongy iron, with its carbon in its further descent, is subject to the oxidising and reducing influences of the carbonic oxide and carbon dioxide, and in the middle region these almost balance each other, so that little change takes place so far as the iron is concerned. In the lower part of the furnace, the residual iron oxide is reduced, probably by cyanides present, and the metal fuses, dissolving carbon, together with silicon, manganese, and phosphorus, which have been reduced in its descent.

The limestone charged in as a flux is reduced to lime, carbon dioxide, CO_2, being expelled, in the upper part of the furnace, when the charge has attained the necessary temperature. When fusion occurs, it combines with the gangue, and produces a slag.

The **silicon** in the pig is reduced from silica (SiO_2) in the charge, in the lower and hotter regions of the furnace; for while carbon does not reduce silica alone, it does so at high temperatures in the presence of iron. The amount reduced depends on the temperature and rate of descent. It combines with the iron, forming a silicide (FeSi).

Manganese is only reduced in the blast furnace by the direct action of carbon at high temperatures. Carbon monoxide only reduces oxides of manganese to the lower oxide, MnO. The reduced metal alloys with the iron.

Phosphorus is introduced into the iron by the reduction of phosphates in the charge, by carbon in the presence of silica at high temperatures. Practically, the whole of the phosphorus in the charge enters the metal, forming iron phosphide, Fe_3P—

$$2Ca_3(PO_4)_2 + 3SiO_2 + 10C = 3(2CaOSiO_2) + P_4 + 10CO$$

Sulphur is introduced in another manner. The sulphide of iron existing in the coke and other materials in the furnace liquates into the iron during fusion, owing to its specific gravity being greater than that of the slag.

By the use of a large proportion of lime, this may to some extent be prevented, and the sulphur carried into the slag as calcium sulphide, the formation of which may be due to a series of complicated reactions at high temperatures.

From a consideration of the above, it will be seen that, to produce a highly carburised iron, time must be given for the metal to take up carbon. These conditions favour also the reduction of silicon, and, in order to keep that element low, more lime must be employed, and a higher temperature will be required in fusion. Hence "grey" irons are freer from sulphur than "white" irons.

It should be noted that in the descent of the charge the whole of the iron oxide is

reduced to metallic iron before reaching the fusion zone, and is therefore incapable of acting as a flux for the siliceous gangue as it does in smelting in hearths (see pp. 44, 164. Lime is not reduced, and this oxide takes its place as a flux.[1] If unreduced oxide of iron arrives at the fusion zone it will enter the slag and produce a "scouring"—easily fusible dark slag. A similar difficulty will result from the extension of the fusion zone, higher up the furnace. This may be caused by the hanging of the charge, which prevents the uniform diffusion of ascending hot gases, and thus prevents their being properly cooled as they ascend, and the charge uniformly heated and reduced.

Alkaline cyanides are produced from traces of alkali existing in the charge by a series of complicated reactions, and accumulate in the lower part of the furnace. They materially assist in the reduction of the last portions of iron oxide.

The first formation of the cyanide may be thus represented—

$$K_2CO_3 + 2C = 3CO + K_2$$
$$K + C + N = KCN$$

The Products of the Blast Furnace

These are (1) pig iron; (2) slag; (3) furnace gases; (4) dust.

Pig Iron.—Pig, or cast iron, is classed as grey, mottled, or white, according to the appearance of the fractured surface. **Grey Pig Iron** has a crystalline or granular appearance, a dark iron-grey colour, is soft and easily turned, chipped, or filed. The carbon, of which it contains a large proportion, has mainly separated in flakes as graphite. Large graphite flakes cause weakness by breaking up the structure while themselves possessing little cohesion. In strong iron the graphite flakes are small.

Grey irons require a higher temperature to melt them than white iron, but are more fluid when molten, and the separation of graphite counteracts to a large extent the contraction that occurs in solidification and cooling. The amount of graphite separating is influenced by the silicon and other constituents. They are specially suitable for foundry purposes. They are weaker than whiter iron, but less brittle. The strength increases as the grain gets finer. They usually contain more silicon and less sulphur than white iron. Grey pig iron dissolves less gas than white, and consequently casts more soundly. Greyness is not a proof of the absence of phosphorus and other objectionable impurities. The carbon varies from 3–4 per cent.

They are classified as Nos. 1, 2, 3, etc., according to greyness, No. 1 being the greyest.

Mottled Iron presents the appearance of a matrix of white iron with grey spots. Its carbon is present in both the free and combined states.

White Pig Iron presents a white, close, and sometimes crystalline appearance. Its carbon is mainly in the combined form (see p. 106). It is extremely hard and brittle, and usually contains more sulphur

[1] The high temperature which prevails ensures the liquefaction of the more difficultly fusible slag thus produced.

ınd less silicon than grey iron. It melts more readily, but flows more luggishly than grey iron, giving off sparks in abundance. On this ıccount it is less suitable for making castings. It contracts slightly ın solidifying. Most varieties pass through a pasty state before

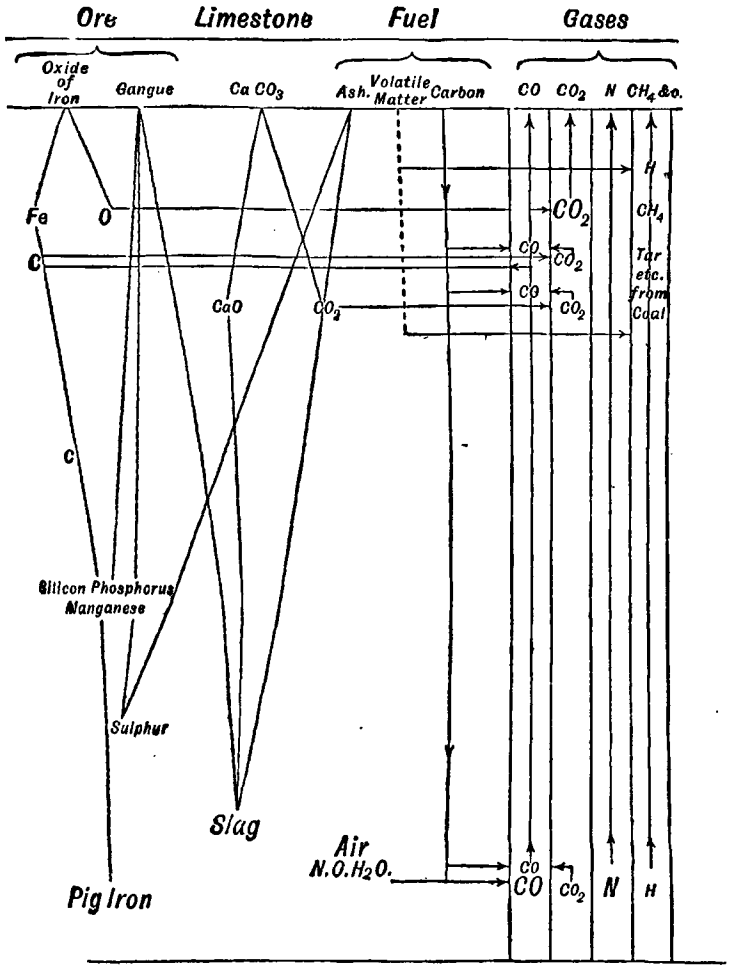


FIG. 79.—Diagram showing chemical changes in blast-furnace.

fusing,[1] in which condition the oxides of iron and slags formed in the puddling furnace can be more readily incorporated with the metal, and the impurities it contains oxidised out with less waste. On this account, malleable iron was formerly made exclusively from irons of this class, either produced directly in the blast furnace, if the ores

[1] All except those containing manganese.

were sufficiently pure, or, if not, grey iron was made in the blast furnace, and afterwards whitened (see Refining, p. 167).

When molten grey pig iron is rapidly cooled, the separation of graphite is prevented, and it is rendered white. On this account Swedish pig, which is cast in thin plates in iron moulds, is often white top and bottom, with a grey interior. The surfaces of grey pigs are often white from the same cause (see Chilled Castings, p. 159). From the larger proportion of sulphur usually present in white iron from the furnace, such irons are classed as **low-grade** irons.

The specific gravity of white iron is greater than that of grey. White has a specific gravity of 7·5 as compared with 7·1.

Grey Forge Pig, produced for puddling purposes, is a class of iron containing less silicon than other grey irons. The amounts of sulphur and phosphorus must be small. It is of fine grain.

Pig irons for trade purposes are usually classed as Foundry, Forge, Bessemer, and Basic pig. Other descriptions indicating the source from which they have been obtained are also used, *e.g.* Hematite iron, etc.

Bessemer pig iron must be practically free from phosphorus, while Basic pig contains that element in considerable quantities.

Cold-blast pig, owing to the lower temperature prevailing during its production, contains less silicon than the hot-blast pig of the same greyness. As excess of this element, owing to its action in precipitating graphite, greatly affects the strength of cast iron, strong castings sometimes contain an admixture of cold-blast pig.[1] Swedish pig, smelted with charcoal, is also used for the same reason.

Spiegeleisen and **Ferro-manganese** are the names applied to varieties of pig iron containing notable quantities of manganese employed for carburisation in making mild steel. Spiegeleisen (German = " mirror iron ") is so called from the brilliancy of its fractured surface. It is highly crystalline, and breaks with broad, flat, lustrous faces, tinged somewhat with yellow. Up to about 10 per cent. of manganese this becomes more pronounced, but as the percentage increases, the size of the crystals diminishes, and in those containing much manganese, the fracture, though yellowish, is granular. Pig containing from about 7 to 30 per cent. is classed as spiegel., and from 30 to 85 per cent. as ferro. (the common contractions of their names). Pig, containing less manganese than would constitute a spiegel, is made for conversion into steel by the basic open-hearth process. This ensures freedom from sulphur and prevents over-oxidation in steel manufacture.

Manganiferous irons are made from manganese ores and spathic ores, containing oxide of manganese, in the blast furnace. The conditions necessary are slow reduction, high temperature, and basic slag. To secure this, light burdens, small blast at high pressure and temperature, densest coke, and much flux are employed.

In making ferro-manganese, the slag often contains as much as 13 per cent. of manganese oxide, and is green in colour. This is necessary to give fluidity to the slag. The make of a furnace working on ferro. is less than when making ordinary pig iron. Manganiferous pig may contain 6 per cent. of carbon.

Siliconeisen and **silico-manganese** are irons containing silicon, or silicon and manganese, but practically free from sulphur, etc. From 12 to 21 per cent. of silicon may be present. They are employed in steel manufacture.

Glazy pig is a whitish crystallo-granular iron, in structure somewhat resembling grey iron, but is brighter and whiter. It contains up to 12 per cent. of silicon.

Small proportions of aluminium, chromium, copper, titanium, vanadium, and calcium frequently occur in pig iron.

Considerable attention is now being devoted to the presence of nitrogen.

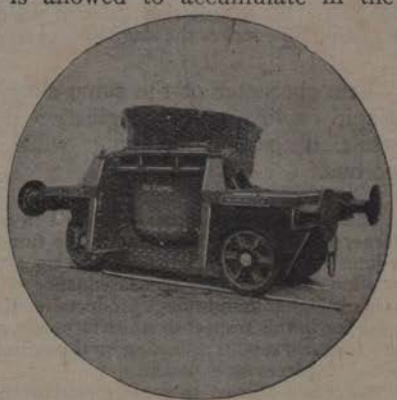
[1] The composition of the iron for a casting can be modified in other ways. Silicon may be reduced by melting steel scrap with the pig in the foundry cupola.

ANALYSES OF PIG IRON.

	Grey.			Mottled.	White.
	Hematite No. 1 (Greenwood).	Cold-blast Bowling (Abel).	Hot-blast Derbyshire ore.	(Bodemann).	Frodingham (Author).
Graphitic carbon	3·045	2·99	3·35	1·99	—
Combined carbon	0·704	—	—	2·78	2·98
Silicon	2·003	0·97	1·51	0·71	0·96
Manganese	0·309	—	1·01		0·505
Phosphorus	0·037	0·5	1·09	1·23	1·41
Sulphur	0·008	0·05	0·02	—	0·28
Iron	93·800		93·02	93·29	93·865
	99·906		100·000	100·000	100·000

Blast-furnace Slag.—In older furnaces, as already noted, the slag is allowed to flow through the slag notch.

In modern furnaces the slag is allowed to accumulate in the furnace and is tapped from the slag notch at intervals. It is allowed to run into ladles on bogies, which are hauled to the tip and discharged while molten by turning over the ladle.



Pearson & Knowles, Ltd., Warrington.]

FIG. 80.—Slag bogie.

Formerly the common way of removing it was to lead the molten slag into slag tubs with movable sides on a rail-track, where it solidified. These were drawn to the slag tip and the slag block removed. The old slag tips are being used for making tar-mac.

The slag usually consists of double mono-silicate of lime and alumina, with more or less magnesia, oxide of manganese, and other bases. The general composition is given below :—

Silica	33 to 47 per cent.
Alumina	5 „ 25 „
Lime	30 „ 40 „
Magnesia	1 „ 8 „
Manganous oxide	1 „ 3 „
Ferrous oxide	1 „ 2 „
Soda	traces „ 1·25 „
Potash	„ „ 2 „
Phosphoric acid	traces only
Sulphur	traces to 2 „

the *general formula* being $3(2CaOSiO_2) + 2Al_2O_33SiO_2$.

Magnesia, ferrous oxide, manganous oxide, soda, and potash may replace part of the lime.

The presence of manganous and ferrous oxides renders the slag more readily fusible. If lime or alumina is in excess, the fusibility is diminished. Magnesia is not such a good flux as lime, giving less fluidity.

In the above, normal slags only have been considered. In making spiegel, more manganese is present, and sometimes, owing to derangements in working or in the making of white low-grade iron, the oxide of iron rises to as much as 8 per cent. Such a slag is known as a *scouring* slag; it is black in colour, and fuses readily. When the accumulating metal comes into contact with such a slag partial removal of the silicon and carbon is liable to occur, the oxide of iron present being reduced with the formation of carbon oxides and silica. The iron is thus rendered less grey or even white.

Blast furnace slags vary in colour from nearly white, through shades of green, blue, or brown, to black.

The green tinge is due to the presence of ferrous oxide. Blue may be due to alumina or alkaline sulphides. The brown colour is ascribed to manganese sulphide. If much ferrous oxide is present, its colour is bottle green or black. Excess of lime makes the slag light coloured and stony.

The character of the same slag varies with the mode of cooling. Rapid cooling makes it glassy; if cooled slowly, it may be stony; while if gas is escaping while molten, it will be light and porous.

The higher temperature employed in making grey iron permits of the use of larger quantities of limestone in the furnace charge. This causes the slag to be lighter in colour—a light greyish slag almost invariably accompanying the production of grey iron. In consequence of the excess of lime, the sulphur in such slags is higher than in slags produced in making white iron, so that grey forge pig is superior in this respect to white forge pig made from the same ore. Moisture and atmospheric conditions acting on the excess of lime present often causes these slags to fall to pieces on exposure.

Slags are utilised to some extent in various ways according to their nature. Certain siliceous slags can be made into blocks for paving, by running the slag into iron moulds, and removing them while still hot into an annealing oven and treating them like glass.

Highly basic slags free from iron are used for making inferior glass.

Excellent concrete bricks, etc., can be made by grinding down basic slags and mixing with about 10 per cent. of milk of lime and moulding the blocks by compression. In course of time they harden like stone. Flags for paving are made by mixing the crushed slag with Portland cement and forming in a hydraulic press. Good cement has also been made from slag. Slag sand is also used in place of ordinary sand for mortar. Strong slags are used for tar-mac and other similar road-making materials.

Slag wool, made by blowing steam through molten slag as it flows from the furnace, is a good non-conducting material. Its use as a steam packing, however, has not been attended with success.

The question of utilising slag is of great importance. For each ton of iron, from 10 to 30 cwts. of slag are produced. This amounts in the aggregate to many thousands of tons yearly, which by its accumulation encumbers the land.

Blast-furnace Gases, as taken off at the throat of the furnace, consist of a mixture of—

Carbon monoxide	25 to 29 per cent
Carbonic acid gas	6 „ 11 „
Nitrogen	54 „ 57 „
Hydrogen	0 „ 7 „
Marsh gas	0 „ 3 „

In furnaces using charcoal and coke, hydrogen and marsh gas are low, being derived almost entirely from the moisture in the air blown in. Ammonia and tarry matters are also present in the gases from furnaces burning coal. At some iron works these are recovered before burning the gases.

It will be observed that the composition of these gases is similar to producer gas, with a considerable increase in the amount of CO_2 present. The furnace may, in fact, be considered as a huge gas-producer. The excess of CO_2 is accounted for by the reduction of the oxide of iron going on in the upper part of the charge, at a temperature too low for it to be converted into carbon monoxide by the carbon with which it is in contact.

The volume of gas is enormous. Each ton of coal burnt yields nearly 4 tons of gas, measuring 130,000 cubic feet or more according to the temperature. A ton of coke yields from 7 to 8 tons of gas.

Dust.—The dust carried over by the gases consists mainly of fine particles of ore, flux and fuel. Very elaborate appliances are in use for the recovery of dust, including dust-catchers, filters and high-tension electrical discharge devices. The dust removed from the gases before burning them in stoves or boilers is used as a source of potash.

Kish is a separation of graphite which sometimes occurs while grey irons are cooling and solidifying.

Iron Founding

Some castings in iron were produced in very early times. Foundry work in iron first developed in connection with munitions. Early cannon were made in cast iron. The first cast in England was made at Buxted in Sussex in 1543. Ordinary castings were not extensively made in this country till 1702, but were made earlier in Germany and Belgium. Rapid developments took place after the introduction of coke in place of charcoal as fuel in the blast furnace. Abraham Darby made this a success in 1713, and Coalbrookdale became a famous cast iron centre producing the first cylinder castings for Watt's engines and the famous bridge " Ironbridge " over the Severn. The latter was built in 1779.

As noted on p. 14, the fitness of a metal for making castings depends on its fluidity when melted and its behaviour during cooling and solidification. The temperature to which a metal must be heated to run well for casting purposes depends on (*a*) the melting-point, and (*b*) the amount of superheating necessary to enable it to become quite fluid and fill the moulds into which it is run.

The pouring temperature will determine (1) the severity of the action of heat on the material of the mould; (2) the amount of heat to be dissipated as the metal cools, solidifies, and cools down finally; (3) the amount of contraction taking place while in the liquid state

—the contraction in the solid state is determined by the melting-point and the coefficient of expansion of the metal; and (4) the length of time occupied in cooling down, *i.e.* the rate of cooling, and thus the length of time the metal remains in the weak hot condition. High latent heat produces a similar effect.

Metals with high *latent* heats like aluminium cool down less rapidly than metals with low latent heat, as, during solidification more heat is given out and must be conducted away. The effects on the moulds may be considerable. In materials of low conductivity expansion of cores (enclosed parts) may be increased before or just when solidification is completed and produce fracture or weakness.

The contraction on solidifying will largely influence both strength and accuracy of detail, the metal withdrawing itself from the fine lines of the mould. Metals which pass directly from solid to liquid are most suitable.

Contraction in the solid state is dependent on the expansibility and freezing temperature (melting-point). Given similar physical properties, low melting-point and a low coefficient of expansion are favourable. Both reduce the contraction.

This enables not only greater accuracy of form and dimensions to be maintained, but reduces the inherent difficulties in foundry work—distortion and weakening or fracture during solidification and cooling.

Distortion.—If parts of a casting are of unequal thickness the unequal rate of cooling introduces stresses which weaken the casting. These naturally increase with the temperature at which they begin —the M.P.—and in some cases cracking or fracture may occur.

Metal surrounding a core may fracture in the hot weak state as it cools and contracts, unless provision is made for the core to yield to the pressure exerted.

Note.—In 1906 Prof. Turner showed that grey iron free from phosphorus showed marked expansion at two points during cooling. With grey hematite one occurred immediately the metal became pasty, and the other at 695° C.

Phosphoric iron of high silicon content showed three such points. The first was considerable, the second slight, and the third at 730° C. was larger than either. These experiments were carried out in ½-inch square bars. These changes affect the various parts of castings of varying thickness at differing periods owing to the difference in the rate of cooling. Further, the first expansion will be utilised in keeping the thinner part of full size by feeding it; and as the final contraction of the metal in all parts is the same, the thicker parts will exhibit a greater apparent total contraction. How far this is compensated for by any expansion taking place after solidification will differ with the composition of the metal. Highly siliceous phosphoric irons apparently expand most, while in ordinary strong foundry mixtures the first expansion is most clearly defined.

Expansion during Solidification and Cooling.—On p. 106 it was noted that graphite separates from suitable irons during solidification and cooling. Since the gravity of graphite is 1·3 and that of the molten iron 6·5 (approximately), it will be seen that the separating graphite occupies (approximately) 5 times the volume of the

metal from which it separates. It must, therefore, tend to produce expansion. The *final* result will be the net balance of the effect of the contraction due to solidification and cooling, and the expansion produced by the separation of the graphite. In some cases there is no reduction in volume. This may occur with very grey iron. See Malleable Castings, p. 161.

The value of this effect in the production of accurate and detailed castings free from distortion and internal stress is obvious.

Unfortunately the separation of the graphite lowers the tenacity. The coarser the flakes the weaker the metal.

This separation, however, softens the metal.

The **method of solidification** must be taken into account. Simple metals and mixtures which form solid solutions offer little difficulty.

Cast iron and metal mixtures which solidify piecemeal by the separation of compounds, solid solutions, and the formation of eutectics, offer a more complicated problem.

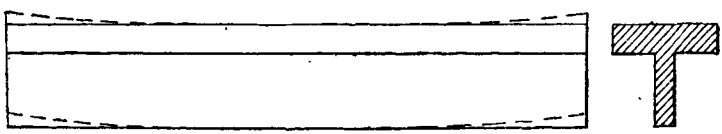


FIG. 81.

As the solidified portion separates, it contracts; and unless provision is made to keep the mould full, cavities will be formed and the casting will be unsound. Hence "feeding" is resorted to. A clear way into the mould is maintained through a feeding head by a pumping rod, and fresh metal added to keep the interior of the casting full. If this be not done, irregular contraction of the casting may take place and it may be "drawn," showing hollows and distortion in places.

Some peculiar effects may result also from irregular solidification brought about in this way. Long and flat castings are liable to be bent and warping of parts of castings may occur. A long casting of the section shown would become hopelessly concave, as indicated, unless provision be made to counteract it (Fig. 81). This is due to the fact that as the thin rib cools and solidifies, it feeds itself from the thick portion till quite solid. It cools down more quickly than the thick part which goes on contracting after the thin rib has become rigid. This differential contraction tends to pull the ends together and bend the casting. This is counteracted in practice by using patterns bent in a manner opposite to the warping, so that the casting shall pull itself straight, or the moulder takes other precautions to avoid warping. The same principle operates in other cases of inequality with results varying with the shape and nature of the casting.

Those irons with least contraction give least trouble, and hence the

greyest iron possible for the purpose is used where difficulty is anticipated.

When cast iron solidifies there is always a tendency for the metal to be disposed with the long axes of the crystallites at right-angles to the cooling surface, *i.e.* the direction in which the heat is conducted away. This is more marked with rapid cooling. The effect on the strength of the casting may be very marked.

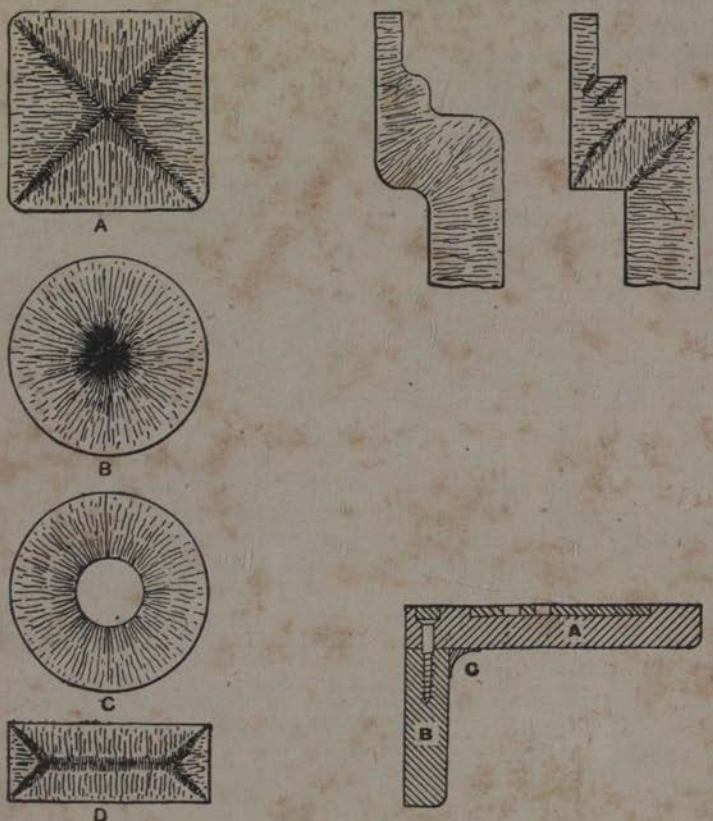


FIG. 82.

When two cooling surfaces are at right-angles to each other and the removal of heat is equally rapid in both directions, the metal inclosed by those sides will solidify so that the portion in a line bisecting the angle will be influenced at the same time from both sides. Crystallisation becomes confused and a line of weakness results. Other causes also contribute to this weakness.[1] Fig. 82 shows the effects in square and in round castings.

[1] Evolved gases and eutectics are forced during the solidification in the same direction.

It will be noticed that while such lines of weakness develop in square faced castings they are absent in round ones and that hollow castings lose the confusion that occurs in the centre of solid castings.

The effect of sharp angles on castings will be noted, and the reason for " filleting," *i.e.* introducing a round fillet in sharp angles.

Fig. 83 shows why hydraulic cylinders are made with round ends.

The illustration shows what occurred when a large hydraulic cylinder with a square end was used (many years ago), and the change when a rounded end was substituted. The flat end actually blew out, but the rounded end stood up to the work.

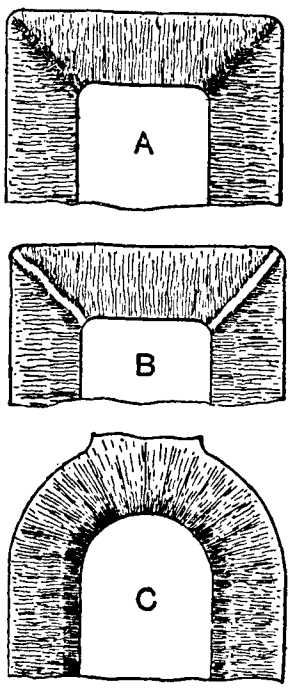


FIG. 83.—A, cast with square end; B, burst in use; C, round-ended.

TESTS.—In practice careful determinations of running power and contraction are made in addition to a careful control of the composition of the iron used.

Tensile and transverse tests are also employed. The latter are carried out on bars supported on supports a fixed distance apart and loaded in the exact middle. The usual size is a bar 2 inches by 1 inch, 42 inches long, supported at points 36 inches apart. Good cast iron will carry from 28–40 cwts. and bend $\frac{5}{16}$ to $\frac{3}{8}$ inch before breaking. The Admiralty test-bar is 18 inches by 1 inch square carried on 12-inch centres. It must carry a load of 2000 lbs. without breaking. The test bars must be true to size and sharp castings.

The tensile strength may vary from 8–12 tons for ordinary iron castings, but special types may exceed 20 tons.

Castings may be made by metal taken from the blast furnace direct, the product being controlled or such additions made as may be necessary to produce metal of the composition desired. This is now being extensively done in the production of pipes, columns, and ordinary castings.

In some cases the metal is removed from the blast furnace in ladles and transferred to furnaces heated electrically or otherwise, and retained or treated as necessary till required for use.

In most cases the pig iron is melted in cupola, reverberatory (air), or regenerative furnaces. On account of economy cupolas are most commonly employed, other types of furnace being used for special purposes such as chilled rolls and malleable castings.

Foundry cupolas are simple blast furnaces more or less similar to Fig. 35. The blast is provided by Roots blower or some type of

fan. A pressure gauge enables the air supply to be regulated. Such furnaces only work intermittently as required. A bed of coke on the bottom and rising above the tuyères warms up the furnace. The charge is introduced with alternating layers of coke and sufficient limestone or other flux[1] to flux the sand, etc., adhering to the pig iron.

Each charge is weighed and consists of the various brands of pig, scrap, and other materials—mild steel or special alloy metals—in weighed proportions, the weight of each charge being adjusted to suit the diameter of the cupola and ensure regular melting. Similarly, each coke layer is definitely adjusted for the cupola, it being necessary that, when blowing, the coke layer should serve to melt the metal immediately above it, and thus ensure the regular descent of the charge to the combustion and melting zone of the furnace.

When the furnace is filled the blast is turned on, and when molten metal appears at the tap-hole the hole is plugged with clay and the metal allowed to accumulate. When sufficient has melted, it is tapped into a ladle and transferred to the moulds. In some furnaces the metal runs as melted into a receiver in front from which it is drawn for casting.

Further charges are added at the top to keep the shaft full during the period of melting or till sufficient has been melted for the requirements.

It is usual to employ more than one type of pig iron and the foundry or other scrap. This is less important now than formerly when the composition of the pig iron was problematical and only judged by fracture. It is, however, necessary to mix irons to produce the particular composition desired.

Iron melted in this way may be considerably changed in composition. Silicon and manganese are oxidised and removed to a greater or less extent, and other elements such as chromium are also partially lost. The extent to which this occurs varies with all conditions, type of cupola, volume and pressure of blast, coke ratio, and the character of the irons in the mixture. Maintenance of uniform conditions only can ensure fair regularity in the results. Hence the difficulty of producing consistent results by different workers even when using the same materials.

Beside loss by oxidation there may be a loss of total carbon, owing to the graphite not being completely dissolved when the iron melts. This is possible in very coarse grey iron. On the other hand, carbon may be taken up in the cupola by contact with the coke. Mild steel scrap in the melt, under normal conditions of melting, invariably takes up carbon seldom less than two per cent. of its weight, often a little more. This must be allowed for in any calculations of composition of the molten metal. These changes and the fact that the temperature of the metal from the cupola is lower than metal from the blast furnace account for the differences in grain and appearance of iron castings from the pig employed in producing them. The

[1] Fluorspar.

lower temperature gives less time and opportunity for the graphite crystals to grow, while the reduction of silicon content gives less tendency for graphitic separation to take place.

The strength of castings is, therefore, higher than pig of the same thickness, size and composition.

In ordinary good melting the loss of silicon generally approximates to 10 per cent. of the amount in mixtures containing up to 2 to 2·5 per cent. With higher proportions the loss is greater. Losses must be ascertained for each individual furnace directly by analysis if efficient control is to be obtained.

In cupola melting sulphur is generally taken up from the sulphides in the coke. Its effects (see p. 109), for general castings, are harmful. It increases the shrinkage and tends to whiten the iron. Hence good coke must be used.

Melting in air and regenerative furnaces is usually adopted when the composition of the metal must be under perfect control as in the manufacture of malleable castings—especially "black heart" or special chill castings such as rolls. The metal does not come into contact with the fuel, and perfect admixture of the materials and uniformity of the melt can be assured. Any necessary adjustments can be made to secure the desired composition either by increase or diminution of the amount, testing and even analysis of the metal being possible while holding the metal ready for casting.

The general influence of constituent elements on the iron has been noticed on p. 104.

For foundry purposes in ordinary castings apart from carbon, silicon, sulphur, and phosphorus are the most important. The two former influence the behaviour of the carbon present, and thus the grain of the iron as well as its casting properties. Phosphorus (phosphide of iron) by increasing the fluidity causes it to "run" better, fill the mould more perfectly, and produce sharp detail.

Silicon is largely relied on to secure soft machinable and less brittle castings. As noted, p. 108, its influence is to cause the separation of the carbon as graphite, leaving the iron grains purer and softer, since the hardening effect of carbon on iron results from the presence of the carbide (Fe_3C), *i.e.* combined carbon. The more completely carbon separates, the softer the metal. Graphite, however, reduces strength, so that a balance must be struck where strength is of importance.

The following figures summarise the effects of silicon on cast iron:—

Maximum hardness . . .	under	0·8 per cent.
Maximum crushing strength	about	0·8 „
Highest modulus of elasticity . . .		1·0 „
Highest density in mass		1·0 „
Combined crushing, tensile, and transverse strength		1·4 „
Tensile strength		1·8 „
Softness and machinability . . .		2·5 „
Minimum combined carbon .	under	4·0 „

The presence of **sulphur** tends to retard the formation of graphite and counteract the effect of silicon. Its neutralising action varies from 10 to 25 times, and an increase of 0·1 per cent. may require from 10 to 25 times its weight of silicon to overcome its effect (see manganese below). This arises from the fact that sulphide of iron is soluble in iron and is associated with the carbide, probably in combination with it.

It thus tends to retain the carbon in a combined form and whiten the iron with all the attendant difficulties of poor casting qualities, unsoundness, warping, cracked, or internally stressed castings and increased hardness.

Manganese is very soluble in iron. It decomposes the iron sulphide forming manganese sulphide, which is not soluble in iron and segregates into small patches in the casting, thus neutralising its effect in large measure. At the same time manganese may retard the separation of graphite. It also acts as a deoxidiser.

Manganese in moderate amounts produces close irons which take a high polish. They do not pass through a pasty stage in solidifying and when molten show a curiously agitated surface in the ladle.

Phosphorus, while lowering the melting-point and improving the running qualities of the metal, reduces the strength and its presence in strong iron should not exceed 0·3 per cent. as a maximum.

Pellets of phosphoric eutectic found in iron castings by the author have in several cases been found to contain 6·5–6·7 per cent. phosphorus and up to 4 per cent. silicon.

In centrifugal methods of casting, the outer part of the casting is made compact and dense by the still fluid, lower melting-point metal being whirled outwards from the centre.

The phosphide is insoluble in *carburised* iron [1] and as the molten metal cools, its other components crystallise and solidify, carbon perhaps, separating as graphite, and the silicon, sulphur, and manganese remaining associated (in solution) or reacting as indicated above. As the phosphide lowers the melting-point and the presence of the carbon prevents its retention in the solid it remains with the still liquid portion of the metal and whatever the original amount becomes concentrated in those patches. The pure iron—iron phosphide eutectic only—contains 10·2 per cent. of phosphorus, corresponding to 67 per cent. of Fe_3P. Its melting-point is 980° C., and it remains fluid till that temperature is reached. When this eutectic solidifies, the phosphide separates from the carburised iron in the mixture, and produces a peculiar microscopic "herring-bone" structure shown in Fig. 84. In larger masses of metal the subsidence of the fluid interior as cooling and contraction continues may cause internal cavities and expose the crystallisation that has taken place. Fig. 85 is a photograph of such a cavity. Fig. 86 is a photograph showing how solidification in a casting proceeds The

[1] In the solid state.

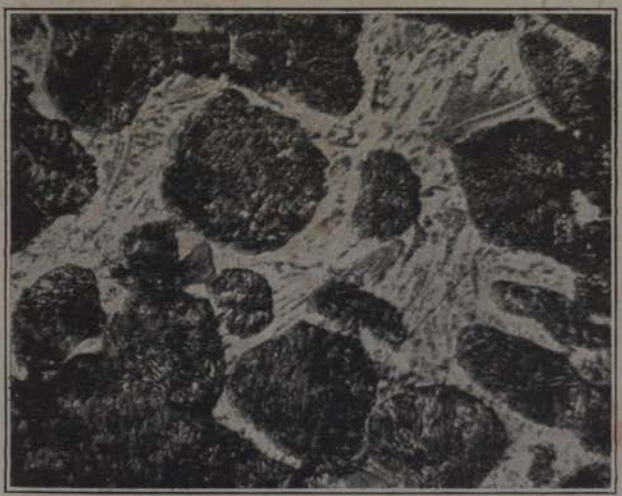


FIG. 84.—White areas phosphoric eutectic moulded on pearlitic grains. ×880.

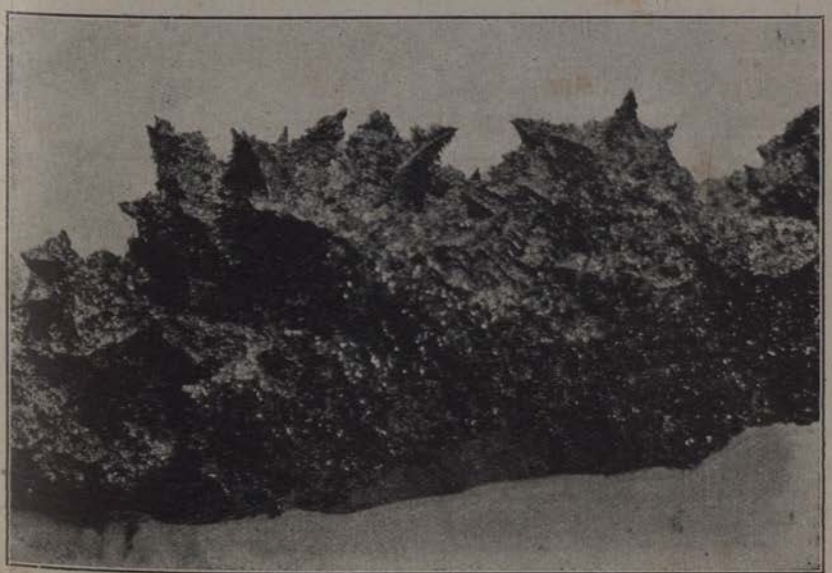


FIG. 85.—Showing exposed crystals in a cavity of an iron casting.

solidifying metal forms a network of crystallites which permeate the whole mass, forming a skeleton sponge, the whole of the pores being filled with the molten material; as heat is lost and solidification proceeds the deposited solid attaches itself to the crystallites, reducing the size of the pores. In this way isolated minute pools of the still liquid portion are formed, which finally occupies the minute cavity in which it is trapped.

Hence the patches of phosphoric eutectic which are distributed throughout the mass (Fig. 84).

FIG. 86.—A mass of crystallites from a "bled" iron casting.

The material of Fig. 86 was a large casting fractured while solidifying. This allowed the molten matter to flow away and expose the crystallites.

Semi-steel—a name sometimes used to designate metal produced by melting down pig iron with mild steel scrap—shows the effect of phosphorus even more definitely than ordinary cast iron.

Moulds for castings may be made in various materials; in sand or loam, metal or other medium.

Sand and loam, being granular or plastic in character, are suitable for packing round a pattern or shaping by special means.

The sand must be refractory to withstand the high temperature and "bind" when rammed in a moist state sufficiently to bear the necessary handling. It must also be porous to permit the escape of gases. This is aided by various "venting devices."

The moulds may be made in " boxes," in two, three, or more parts, sand being rammed round a pattern by hand, compressed by mechanical means (moulding machines), or jolt rammed by shaking on a jolt machine.

Hollow parts are produced by means of " cores," separate parts of the mould which are suitably supported by " core prints " or by " chaplets," " studs," or by other means in the desired position so that the metal may flow round. The mould is divided to allow of the removal of patterns, " partings " being selected to enable this to be done.

The sand as rammed contains approximately 13–15 per cent. of

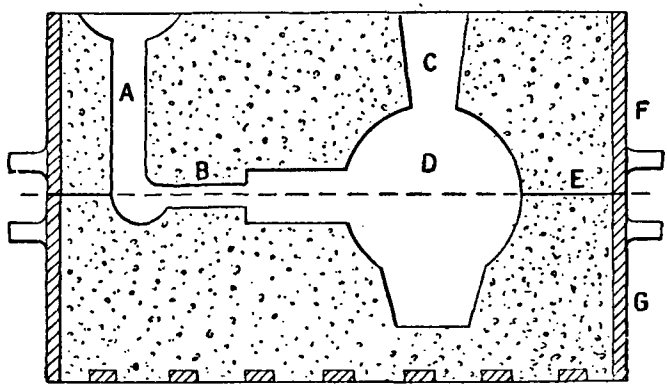


FIG. 87—Simple mould. A, gate; B, runner; C, feed-gate and riser; D, casting; E, parting; F, cope; G, drag.

moisture. For most purposes the metal is run into the moist mould. For important work or where special moulding difficulty occurs the moulds are " dried."

The former is " Green sand " and the latter " Dry sand " moulding. In either case the surface of the mould is protected by a layer of " blacking " (graphite or other matter), or in some cases by soapstone or other infusible matter to increase the refractoriness or improve the surface. Moulding sand and moulding materials for iron always contain an admixture of coal-dust or other carbonaceous material. The gas evolved by contact with the hot metal serves to keep the metal from the pores and protect the surface from the heat. It also aids the flow of the metal.

Cores are made of suitable moulding sand, loam, or mixtures of sea or other silica sand mixed with oil, core gum (dextrin) or other agglutinant and carefully dried. It is necessary that they shall be specially vented to allow gas to get away. Iron supports are often embedded for strengthening purposes. Entire moulds are sometimes

made in the same manner. Such castings are described as "core" cast. Greater accuracy and improved quality are obtained.

Loam is a plastic refractory sand and clay mixture used in the state of mud and plastered on brickwork or other support to a depth which enables it to be shaped by strickles—shaped boards moving in a circular sweep or sliding along "guides." The loam is dried out before casting. Special care is taken to strengthen and support the mould. Most important heavy work is done in dry sand or loam. Sometimes patterns are used in loam moulding.

Plate Moulding.—Patterns are sometimes fixed on a plate in a position which forms the best parting plane and thus facilitates moulding. The plate is placed in position (on an oddside) and the "drag" lower side rammed up. On turning over the pattern and drag the cope (top side) may be rammed on the top. When the pattern plate is removed the two parts fit perfectly, forming the complete mould.

Plates or similar means of producing "partings" are used on machines.

Gates and Runners.—In making a mould provision is made for running in the metal. The vertical hole through the cope into which the metal is poured is the gate (or git), and may deliver the metal directly to the mould or have side channels from the bottom leading to the mould cavity—the runners or spray.

Other openings rising to the surface from the top of the mould are sometimes provided to enable the air and gases to get quickly away; they also serve other purposes. They are known as "risers," and may serve as "feed gates." See p. 147.

Special casting methods are sometimes employed. In **centrifugal casting** the moulds are mounted on revolving tables, the centrifugal effect forcing the cooling denser metal to the circumference of the circle of revolution.

Spun pipes are cast in a machine in which the mould—a permanent mould—is mounted to revolve horizontally. Metal poured into a receptacle mounted at the open end is conveyed by a long spout to the further end of the mould. The latter as it revolves travels slowly at such a rate that the entering metal forms a layer of the desired thickness which extends ultimately from end to end. The pipes on removal are annealed.

Heavy castings are often made in the foundry floor, pits or a sufficient depth of material being provided.

Moulds require to be well secured to prevent the tops being lifted by the fluid pressure of the head of metal in the gates or bursting. Fastening or weighting of the cope is necessary, and if necessary, proper supports or embedding in sand in the case of deep loam moulds.

Castings are allowed to cool down in the mould or removed as soon as quite solid, according to size and requirements. Cooling slowly in the hot mould may have considerable effect on the structure of the metal. Gates and risers are knocked off as soon as possible after solidification, while the metal is red hot and weak.

With heavy castings, when deep gates are employed and the metal enters at the bottom of the mould "bottom gating," this cannot be done.

With important castings, test pieces or bars may be cast on the casting itself and subsequently detached.

Faults in Casting.—*Warping* has already been alluded to. It is prevented by suitable modification of the patterns, by precautions in moulding, attention to design in distributing weight, and selection of a suitable type of metal.

Scabbing is the production of rough or warty excrescences on the surface, resulting from portions of the mould face being detached and floated or washed away by the hot metal, generally due to faults in moulding or sand mixing.

Sand burnt castings have a thick crust of sand firmly adherent to the casting, the metal having run round and enclosed the grains. This is due to sand being (*a*) not sufficiently refractory or properly blacked for protection; (*b*) too open in grain; (*c*) metal too hot. Sand burnt castings are difficult to dress and machine.

Skin chilling produces a thin layer of "white" iron on the surface, extremely hard and brittle and difficult to machine. See p. 142. It results from sand being too wet or badly blacked or even lacking carbonaceous matter.

Blow Holes.—*Porosity* and *unsoundness* result from various causes. Blow holes are included bubbles of gas and are smooth inside. The gases may be given out by the metal, or expanded air from the pores, or gas generated by contact of the hot metal with moisture or carbonaceous matter. They should escape from the mould either by the openings in the cope or through the "vents" provided (p. 154). If bubbles come into contact with solid matter, such as detached pieces of the mould (see scabbing), or solidified metal formed near any surface of the casting they have little chance to escape, and blow holes are almost inevitable. Hence the importance of perfect venting and hot metal and good sand.

Porosity and unsoundness may arise through the fluid contraction taking place as the metal cools to complete solidification with inadequate "feeding." It is necessary to keep up a supply of fluid metal to the heavy parts of the casting. If this fails the subsiding metal as solidification proceeds will expose the iron crystallites and produce porosity. Very hot and fluid metal combined with well-placed and properly attended feed gates minimise the trouble.

In cases where it is impossible to deal with the trouble in this way "denseners" or "chilling plates" are employed. These are iron plates of suitable shape which are embedded in the mould face at the places where difficulty is anticipated. They are well blacked and the thickness ($\frac{1}{2}$–$\frac{5}{8}$ inch or more) is insufficient to produce actual chill, but facilitates the local cooling of the metal at that point. This ensures solidity by shortening the period of complete

solidification in the neighbourhood and ensures the full local feeding while the metal is fluid.

Hard Spots and Pellets.—Hard spots are often chill effects due to too much moisture in the sand or some local cause. Pellets are probably of two kinds. Small drippings of metal falling into the mould may solidify immediately and be carried forward and embedded without being assimilated by the metal. In solidifying a film of oxide of iron may form on the surface and prevent the pellet from amalgamating. Other pellets are found in the mass of the casting. They may be loose in cavities or completely or partially filling them.

They consist of the eutectic mixture—highly phosphoric—and often siliceous in character—which remained fluid and entangled in the contracting skeleton of crystallites forming the mass of the casting. This fluid was forced by the contraction into the cavities in which it is found or through the skin into larger cavities as drops. Similar effects sometimes occur at the surface with highly phosphoric irons, the eutectic being squeezed to the surface. Such pellets are hard and brittle. In practice we have found them contain up to 6·7 per cent. of phosphorus and 4 per cent. silica. See p. 152.

Shrunk and sunk castings with hollows in the surface result from the excessive shrinkage of the metal. They arise from causes discussed on p. 152, and are often due to lack of total carbon, or silicon, or of excess of sulphur in the metal.

Castings on removal from the moulds are " dressed " to remove gates, fins, or other metal, adherent sand, cores, and supports, leaving the skin of iron oxide as nearly intact as possible. Small castings are rumbled in a tumbler. Others are sand-blasted to remove sand and improve the surface.

Castings for machining purposes are often " softened " by packing in boxes in iron borings or other material—sometimes oxide or scale—and heated in a furnace above 750° for 24 hours or more. See p. 160.

Sound satisfactory iron castings can only be attained by a combination of good metal and moulding materials, good design, skilled work, and efficient supervision, special attention being paid to the composition and pouring temperature of the metal.

Chilled castings are produced by using iron moulds for the part of the casting it is required to " chill." As noted (p. 142), cast iron of suitable composition can be converted into white iron when rapidly cooled from fusion. The surface of a casting is in this way made almost glass hard. This provides a means of producing durable wearing surfaces while the body of the casting remains grey, soft, and tough, with the greater soundness and strength accompanying that condition. Reference to the properties of white iron, its sluggishness in running, excessive contraction and consequent unreliability of castings of varying thickness, together with the pasty condition through which it passes in solidifying make it an unsuitable metal for castings to be used in the condition " as cast."

The effects of various elements on the behaviour of the carbon have

already been dealt with. Any cause tending to the separation of graphite or to retard the cooling will tend to produce a coarser, greyer structure, and vice versa.

The presence of elements which tend to prevent the decomposition of iron carbide increases the depth of chill and may influence the amount of other elements necessary to ensure greyness in the body of the casting.

It follows that irons suitable for chilling must contain sufficient silicon to make the unchilled metal grey—in proportion to the mass of the casting—and be low in sulphur and phosphorus. A suitable iron for heavy castings would contain approximately 1–1·2 silica, not more than 0·1 sulphur, 0·3–0·5 phosphorus, 0·6–0·7 per cent. manganese.

Note.—All castings for malleablising are made in white iron. Special care in design and treatment has to be taken to avoid these troubles, which are partly neutralised in conversion to malleable.

"Chills" are the iron moulds used, see Fig. 88. They are often in sections. The depth of the chill depends on the weight of the chills employed. For deep chilling, as in making chilled rolls, the weight of the chills may be much heavier than the metal to be chilled. The chills are of fine-grained cast iron and require careful preparation and care.

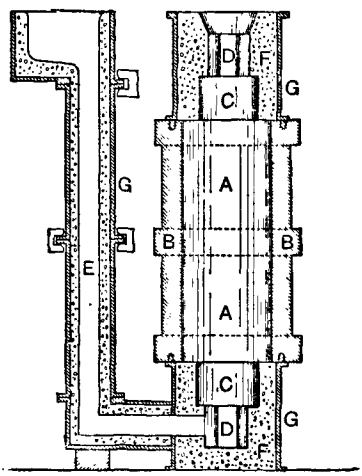


FIG. 88.—A, body of roll; B, chill; C, neck; D, wobbler end; E, running-gate; F, sand mould; G, boxes.

Rolls for rolling iron, zinc, and other metals, rubber mixers and calenders, grinding plates, and many other castings are made in chill. Treads of railway and car wheels are chilled in U.S.A. The ends, necks, and bodies of the rolls remaining grey are machinable and tough, the white surface layer passing through white mottled, grey mottled to grey in the interior. The transition just referred to prevents cracking off of the hard layer.

MALLEABLE CASTINGS

Malleable castings differ from ordinary castings by being less brittle and generally stronger. Thin ones may be bent and twisted without breaking. Modern methods produce castings attaining a tensile strength of 23–25 tons.

These castings are made in white iron—brittle and unmachinable—

and subsequently made soft, tough, strong and machinable by treatment.

White iron of suitable character runs perfectly when sufficiently heated, but superheating increases *fluid* contraction and the inevitable pasty solidification and high *solid* contraction of white iron also takes place. Hence the necessity for minimising troubles arising from these causes by attention to design.

Two types of malleable castings are made:

White heart castings.

Black heart castings.

When cast iron is molten the carbon is in solution as iron carbide, and unless separated as graphite remains in combination in the solid metal.

White heart castings are decarburised, thus removing the hardening element.

Black heart castings retain the carbon, but in the free state. See p. 105 on the effects of carbon.

White Heart Castings.—Raumer castings.

No castings for malleablising should contain graphite. This is especially important with black heart castings.

The metal is decarburised by packing the castings in suitable boxes of iron or of steel alloy—embedded in granulated oxide of iron—hammer-scale, red hematite or similar material. This both effects the removal of the carbon by oxidation during the process and provides an adequate support for the castings while hot, preventing distortion.

The boxes are packed firmly and transferred to the annealing oven or furnace. The temperature must be uniform within 50° C., and is maintained at from approximately 900° to 1000° C., dependent on the quality of the iron and the nature of castings, for a period of say three or four days. The extent of the decarburisation depends on the thickness of the castings. Thin ones are decarburised through. With greater thickness a layer of decarburised metal is succeeded by partially decarburised layers leading to an interior in which the carbon contents are little reduced, but in which much of the carbon is free as " temper " graphite. The change in a casting may be appreciated by the analysis given below from author's note book.

	As cast.	After once annealing.	After twice annealing.
Carbon	3·48	0·43	0·1
Silicon	0·59	0·61	0·62
Manganese	0·59	—	—
Sulphur	0·11	0·15	0·16
Phosphorus	0·28	0·29	0·30

The carbide has been transmitted by diffusion from the interior towards the oxidising material by which it is surrounded and oxidised.

It is essential in this method that the carbide shall not decompose at a temperature at which the operation is conducted, and careful control of the temperature is necessary, see *pyrometry*. In the case given above, the temperature did not exceed 1020°, the decomposition temperature of the carbide being about 1100° C. High sulphur contents sometimes are employed to prevent such decomposition and ensure diffusion of the carbide generally by makers who have not the means of efficient chemical and pyrometric control.

Such castings corrode more rapidly than ordinary castings.

Black Heart Castings are so called because of the dark grey aspect of the casting on fracture.

The carbon in the original casting is not removed but separates as temper graphite during the annealing treatment. This separation not only leads to softening of the metal, but the thrust of the liberated graphite due to the increase in volume gives relief to internal stresses set up during the solidification of the white iron casting. Similar relief is assured in the treatment of ordinary castings in softening by the decomposition of the carbide of iron which renders them hard.

In some cases actual permanent increase in volume may occur.

NOTE.—Carbide of iron, Fe_3C, does not decompose below 1250° C. in the presence of iron alone under normal conditions even on prolonged heating.

The presence of other elements influences the temperature at which this takes place. Silicon lowers it while sulphur and manganese raise it. Low sulphur irons containing from 0·75–1·0 silicon can be annealed as black heart castings at from 740–760° C. but with lower silicon and higher sulphur, a temperature of 900° to 950° is necessary.

Charpy and Grenet found that with iron containing less than 0·02 per cent. sulphur the separation of temper graphite commenced with—

0·07	per cent.	Si at	1150° C.
0·27	,,	,,	1100° C.
0·80	,,	,,	800° C.
1·25	,,	,,	650° C.

on prolonged heating. With 2·1 silica, 85 per cent. of the carbon became graphitic with 6 hours' heating. It was further observed that once the separation had begun it could in most cases be further continued at a lower temperature.

Most cast irons show a critical point about 700° as does steel. With the amounts of silicon in the table given above they showed another point at temperatures varying from 1140°–1165° C. on rising and 1120°–1145° on a falling temperature.

It follows from the above that it only becomes necessary to maintain irons of approved composition above the required temperature to separate the carbon and produce strong soft castings.

The castings are packed in suitable material, sometimes oxide—though not for oxidation purposes—iron borings, or inert material

like ganister, and heated under close supervision and control at temperatures suitable to metal of the composition employed.

Sometimes when oxide is employed a thin layer of decarburised metal is produced at the surface.

In most cases the whole of the carbide is not decomposed, and as much as 0·9 per cent. of carbon may remain in the casting as carbide.

No graphite should occur in the original castings if the best results are to be obtained.

When malleableised, the finished castings are often larger than the original castings. This depends on the nature of the iron employed and the treatment followed. Graphite separates gradually while the iron is hot and expanded, and prevents contraction to the original size.

Pearlitic cast iron and castings are produced by casting suitable iron into warm or heated moulds of the ordinary poor conducting type (see p. 154) to retard cooling.

CHAPTER X

MALLEABLE OR WROUGHT IRON

UNDER this heading are included all classes of iron which can be hammered and forged at red heat, and are not hardened by heating to redness and plunging in cold water. It is usual to further restrict the term to the metal as obtained in a pasty, unfused state, produced either in a direct manner from the ore, or indirectly from pig iron by puddling or analogous processes.

Direct Processes.—As previously noted (p. 138), iron oxides are reduced by carbon or carbon monoxide at dull-red heat, and the earthy impurities can be removed, and carburisation prevented, by allowing oxide of iron to pass into the slag. Such a slag is readily fusible, and by hammering the pasty mass obtained, the particles of malleable iron become welded together, and the slag is expelled. All the iron produced by the ancients was thus obtained, and many processes of a similar character are yet in use in India, Burmah, Africa, and other places, where modern civilisation and its methods have not yet penetrated.

Various modern "direct" processes for the treatment of special materials, and with a view to the saving of fuel, have also been introduced. Methods of the crudest and of the most refined nature belong to this category.

In Burmah, a hole in the side of a clay bank, some 10 feet deep and 2 feet wide, does duty for a furnace. The front of the bank is strengthened by small branches interlaced and supported by stakes driven in the ground. At the bottom, an opening about a foot high and the width of the furnace is cut through the bank for the removal of the lump of metal and the slag. This is stopped with clay. A row of clay tubes, about 4 inches long, made by plastering clay on bamboo, and afterwards drying and burning them, is introduced about halfway up the opening. These supply the air to the furnace, which works entirely with natural draught. A fire is lighted, and a quantity of charcoal thrown in. The rest of the furnace is filled up with alternate layers of ore and charcoal, and the furnace is left pretty much to itself. In a few hours slag makes its appearance at the bottom, and is tapped out and examined. If free from shots of iron, it is thrown away. When the furnace has burnt out, the clay breast is broken down and the lump dragged out. It consists of metal, fragments of unburnt charcoal, and slag, and weighs about 90 lbs. It is broken up and sorted, according to fracture, into soft, and hard or steely iron.

In India, most native iron-makers used blast, and the furnaces are generally built above ground. They range in size from a chimney-pot to about 10 feet high, and the blast is supplied by curious contrivances; bellows made of goat and bullock skins stripped off whole, single-acting wooden blowing-cylinders, the pistons of which are stuffed with feathers, and bellows not unlike ordinary smithy bellows, being employed. In some furnaces, the front is broken down in order to remove the iron; but in others the metal is hauled out by tongs from the top, a fresh charge being at once introduced.[1]

Similar processes are in use in Central Africa.

Easily reducible brown hematites containing over 50 per cent. of iron are the ores generally employed. Little more than half the metal is reduced, the rest passing into the slag. The presence of so much oxide of iron in the slag prevents the reduced metal from taking up carbon, and, in many cases, the low temperature which prevails is unfavourable to carburisation. The silica and phosphorus in the ore are removed in combination with oxide of iron in the slag.

The famous **Catalan, Elba,** and **Corsican** processes are very similar. They still survive to a small extent.

FIG. 89.

The forge (Fig. 89) in which the reduction is effected is a rectangular hearth, one side of which curves outwards at the top. It is about 21 inches long, 19 wide, and 17 deep. The bottom is a movable block of granite. The tuyère side is built of malleable iron blocks, as also is the sloping side facing the tuyère; the back is of masonry, and lined with fire-clay. The front consists of thick iron plates, placed edge to edge, the lower end being on the ground. The tuyère is of copper, and the blast-pipe lies in it loosely. It is inclined so that the blast strikes downwards. A tap-hole at the bottom serves to remove slag, and to introduce a bar to lift up the mass of iron when the process is completed.

The hearth, hot from previous working, is filled with charcoal to the tuyère, and a gentle blast turned on. When fairly alight, a broad shovel is placed a little in front of the tuyère, so as to divide the hearth into two unequal parts.[2] The tuyère side is filled with charcoal, which

[1] Modern blast furnaces are now in use in India.
[2] After charging this is removed.

is moistened. On the other side the charcoal is rammed down tightly, and the space filled with roasted and broken ore, from which the fine stuff has been riddled. This is then covered with a mixture of fine ore and charcoal dust, and finally with moistened charcoal. The blast is then turned on, and in a few minutes the flame of carbon monoxide makes its appearance at the top. From time to time ore and charcoal are added, being pushed down the sloping side of the furnace into the hearth, under the tuyère, where the reduced iron accumulates. The charcoal is repeatedly damped to prevent its too rapid combustion. The slag is removed at intervals and examined. The operation is complete in five or six hours. The lump collected at the bottom is raised in front of the tuyère for a few minutes to raise it to a full heat and melt out slag, and is then dragged from the furnace, and hammered to expel slag. It weighs about 3 cwts.

The mass, which is never homogeneous, is broken up and sorted. The pieces are reheated in the corner of the hearth formed by the tuyère side and back, during the progress of a subsequent operation, and drawn down into bars.

The reduction is effected principally by the carbon monoxide CO, formed by the air passing through the carbon before coming into contact with the ore, consequent on the method of filling the hearth, and the downward direction given to the blast. The siliceous impurities are fluxed off by ferrous oxide formed by partial reduction of the ferric oxide in the ore. A very fluid, fusible slag is thus obtained, carburisation at the same time being prevented. This is also favoured by the low temperature employed.

The blast is provided by a water blowing-machine known as the *trompe*, and the pressure varies from ½ to 1½ lb.

The American bloomery formerly in use in Canada and the United States was a furnace of similar type operated in much the same way. In New Zealand and Canada it was used for the treatment of titaniferous iron sand.

It was usual to slightly heat the blast by passing it through iron pipes in a chamber over the bloomery. They made a ton of blooms per day working continuously.

These methods, if not obsolete, are in use only to a very limited extent.

The operation of bloomeries in the United States ceased in 1901.

Note.—Ores containing more than 9 per cent. of titanic oxide are very difficult to smelt in blast furnaces. Hence ilmenite is not included as an iron ore.

Indirect Methods.—Pig iron is converted into malleable iron by removing the silicon, carbon, manganese, and phosphorus by oxidation. During this treatment, part of the sulphur is also removed if the slag produced is highly basic.

The above-mentioned bodies have a greater affinity for oxygen than iron has, and hence, on exposing the metal during fusion and while melted to a blast or current of air, they are oxidised, together with a portion of the iron itself, which forms such a large proportion of the whole.

The silica (SiO_2), phosphoric anhydride (P_2O_5), manganous oxide (MnO), and oxide of iron formed, unite together, producing a fusible

slag consisting of silicate and phosphate of iron, with an excess of iron oxide. The carbon passes off in the gaseous state as carbon monoxide or dioxide.

Instead of using atmospheric oxygen, the oxidation may be brought about by heating the pig iron with oxide of iron or substances containing it, such as red hematite, hammer-scale, best tap-cinder, etc. The iron oxide gives up a portion of its oxygen to the impurities, and they are removed into the slag.

Practically the same thing occurs when an air blast is employed, owing to the large excess of iron present. The oxygen forms mainly oxide of iron, which is subsequently decomposed by the silicon, etc., present.

Upon these principles all processes for the conversion of pig iron into mild steel and wrought iron depend. The essential difference lies in the fact that while *mild steel* is obtained at the end of the process in a *molten* state, and is run into moulds, *wrought iron* is obtained in an unfused, *spongy* condition (owing to the lower temperature that prevails), the particles of iron being subsequently welded together.

The order in which the impurities in the iron are attacked varies with the working conditions of the process, the principal conditions being the temperature and the composition of the slag.

Silicon, manganese, phosphorus, and carbon all oxidise before the iron, but the exact order of attack varies with the temperature. At very high temperatures carbon oxidises, although silicon and manganese have not been completely removed, and at low temperatures with a highly basic slag phosphorus may be oxidised before all the carbon has been removed.

In the Bessemer process, silicon and manganese are oxidised until the temperature has risen to such a height as to make the carbon chemically active when the oxidation of the carbon proceeds rapidly.

In the Basic Bessemer process phosphorus remains after the carbon has been eliminated.

In cases where the metal is not fluid and not agitated, the oxidising influences may be local and overlapping occurs.

Sulphur is not removed by oxidation, but is taken up by the slags, apparently by liquation, as sulphide.

Processes for producing wrought iron by subjecting pig iron to a blast of air in hearths are known as **finery** processes ; those in which it is treated with oxides of iron in a reverberatory furnace, as **puddling.**

Wrought Iron.—All kinds of pig are not equally suitable for conversion into malleable iron. Only some 80 per cent. of the phosphorus present, and 40 per cent. of the sulphur, are removed in finery and puddling processes. The presence of too much silicon also gives trouble owing to the fluidity of the metal, and consequent difficulty of working, as well as the great loss in weight which occurs, and the large consumption of " fettling." [1]

The pasty stage through which white pig iron, free from manganese, passes prior to fusion, permits of easier mixture with the iron oxides

[1] Oxide of iron, see p. 170.

and oxidising slags in the furnace which effect its purification; and in consequence of its composition less loss occurs. It is therefore preferred to grey iron on this account, but, as its sulphur contents are usually higher, this advantage is often more than counterbalanced. Unless the iron is smelted from pure ores, it is now usual to produce grey pig in the blast furnace, and either treat this directly or subject it to a refining process previous to its actual treatment for malleable iron.

Refining is a process formerly generally employed for the conversion of grey into white iron previous to puddling or blooming.

The refinery or running-out fire is shown in Fig. 90. It consists of a rectangular hearth 4 feet square and 18 inches deep, formed on three sides of water-cooled cast-iron blocks, U U. The front is a

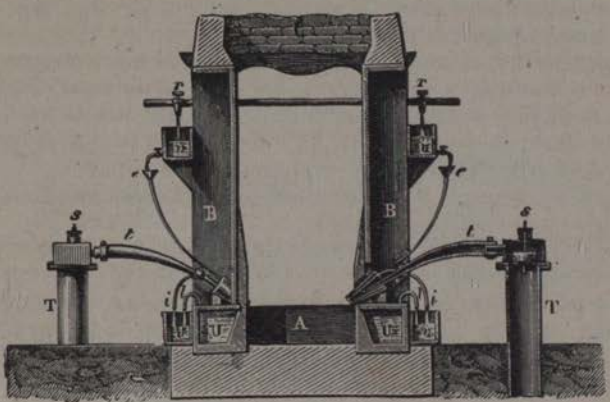


FIG. 90.

cast-iron plate in which the tap-hole is situated. Four columns, B B, situated at the corners of the hearth, carry the brickwork stack—some 16 to 18 feet high—on girders. The bottom is made of sandstone blocks.

The hearth is enclosed by iron plates attached to the columns. Those at the back are hinged, while the front plate is attached to the end of a lever and counterpoised, so as to be easily raised and lowered. The hearth is provided with a number of water-cooled tuyères, usually five or six. These are inclined at an angle of about 30°, and placed on both sides in such manner that the tuyères are not opposite to each other. In this way the blast is uniformly distributed over the hearth. In front is an iron mould for the reception of the metal, and beyond this a pit for the slag, which runs off the surface when the mould is full. Owing to its lower melting-point, it remains fluid longer than the iron.

The blast is employed at a pressure of about 2½ lbs. per square inch.

The hearth, being hot from a previous operation, is partly filled with coke, and the charge of about two tons of pig iron and scrap

introduced, in layers alternating with coke, through the folding doors at the back. Some hammer-scale (Fe_3O_4) is often added. The blast is turned on, and in about a couple of hours the charge is melted down. More coke is added if necessary, and the blast continued for from half to three-quarters of an hour, during which period bubbles of carbon monoxide are seen escaping from the metal and burning on top. The metal, when deemed refined, is tapped out and cooled rapidly, water being often thrown on the surface for this purpose. The plate of metal is from 1 to 3 inches thick.

Owing to the large amount of air supplied, the iron is subjected to oxidising influences during the whole period of the operation, and, when fluid, the downward direction of the tuyères causes the blast to play continually on its surface. The oxide of iron thus formed, and that added as hammer-scale, attacks and oxidises the silicon, carbon, and phosphorus in the metal.

The removal of silicon from the metal in refining is most marked, pig iron containing 5 per cent. being reduced to from 0·5 to 0·7. Carbon is seldom reduced more than 1 per cent., while the removal of phosphorus is very variable. In some cases it is scarcely affected. The rapid cooling ensures the retention of the remaining carbon in the combined form. A white, close, dense metal known as *plate metal*, or *refined iron*, is produced.

The slag consists mainly of basic silicate of iron. In this process sulphur is not removed.

Removal of Sulphur from Pig Iron.—The purification of pig iron from sulphur has received much attention. Manganese and sodium carbonate are both employed for this purpose. In each case, a sulphide not decomposed by iron is formed.

With sodium carbonate, silicon is also largely removed, and some carbon, with separation of metallic sodium. The molten pig was run into a receiver containing the carbonate.

Scheerer proposed the use of calcium chloride and salt as a desulphuriser, by adding it in the puddling process. **Saniter's** desulphurising process consists of running the molten pig into a receiver containing calcium chloride and lime. Fluorspar may also be used.

Much sulphur is eliminated in the receivers used to retain a supply of molten metal for steel making, rising to the surface mainly as manganese sulphide.

Note.—The " washing " process is a method of refining pig iron for steel-making.

Finery Processes.—Welsh Finery, Walloon Process, Swedish-Lancashire Hearth.

In these processes, the pig iron is converted into malleable iron in open hearths, *in contact with the fuel.* In consequence, only charcoal can be employed, coke and coal not being sufficiently free from sulphur.

The Swedish-Lancashire hearth is a small rectangular finery made of cast-iron plates. The top is arched over, and communicates with

a chamber in the flue in which the pig iron is heated prior to being placed on the hearth. The hearth has one tuyère, nearly horizontal, supplied with blast heated to about 120° C., by circulating through iron pipes placed in the flue.

The hearth is filled with charcoal, and the charge of about 2 cwts. of white or mottled iron drawn from the flue, the blast turned on, and the charge melted down. The atmosphere is highly oxidising, and as the drops of metal sluggishly pass before the tuyère oxidation occurs.

The metal collects at the bottom, and slightly hardens. The cake is broken up by the workmen, and held before the tuyère, to be remelted and further oxidised. When the metal gets stiff and infusible, it is raised to the top, fresh charcoal added, the temperature raised, and the whole remelted. As it drops down before the blast into the bath of highly basic slag at the bottom, its fining is completed, and the pasty mass is collected into a ball, withdrawn from the furnace, and consolidated by hammering, the admixed slag being thus expelled.

The Walloon process is similar. These finery processes are wasteful. A loss occurs of from 15 to 20 per cent. on the pig iron employed.

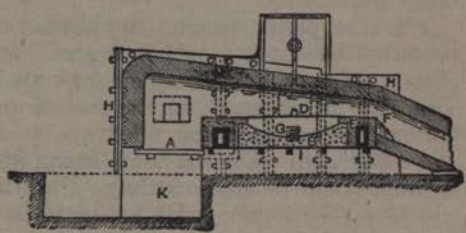


FIG. 91.—A, fire-place; B, bed; C, fire bridge; D, working door; E, flue bridge; F, flue; G, tap-hole for slag; H, plating of furnace.

They are still retained in Norway and Sweden, and were formerly in vogue in South Wales for the production of tin bars for tin-plate manufacture, but are now superseded, tin bars of better quality being made from open-hearth steel at a much reduced cost.

Puddling.—This process—the most important of all methods of making malleable iron—was introduced by Cort, in 1784, as a method of employing coal for fining iron. Up to this period, the sulphur in coal and coke had prevented their use in fineries. The sulphides in the ash being in contact with the metal are dissolved by the iron.

The employment of reverberatory furnaces, in which the fuel is burnt out of contact with the iron, completely overcame the difficulty; the sulphur, being burnt to sulphur dioxide (SO_2), has no effect on the iron under the conditions of working.

Fig. 91 shows a section of a puddling furnace. It is a reverberatory furnace, the grate area of which is large in proportion to the hearth space (1 : 1½ or 2). The bottom and sides of the hearth consist of cast-iron plates suitably supported, and backed with fire-brick. They are protected with some material rich in oxide of iron, and kept cool by the circulation of air under and round them.

Formerly brick beds and sand bottoms were employed. The

working door, in front, is only opened to introduce and withdraw the charge. It slides between guides, and is attached by a chain to the end of a lever, and is counterpoised. The working of the charge is effected through an opening in the bottom of the door (the stopper-hole), through which the bars (rabbles) for this purpose are introduced. In front of the door is a shelf or fore-plate. The interior is lined with fire-brick, and the furnace is supported externally by iron plates and tie-rods. A damper in the flue or at the top of the stack is employed to regulate the draught.

It is essential for the success of the process to be able to produce an oxidising or reducing atmosphere as required.

The fire- and flue-bridges are usually hollow, the circulation of air keeping them cool. These, as also the sides of the hearth, are sometimes kept cool by the circulation of water. Under the fore-plate is a tap-hole, for the removal of slag, which is generally run out every second heat.

The iron plates forming the bottom and sides of the hearth are protected by about 3 or 4 inches of "fettling." Bull-dog, calcined pottery mine, and best tap-cinder[1] are employed for this purpose. They are broken to about the size of macadam, and spread on the bottom, the spaces being filled up by similar material ground fine and moistened. The fire-brick lining above the side plates projects slightly, so as to retain the fettling. **Puddler's mine** (soft red hematite) and blue billy (ferric oxide produced in burning pyrites for making sulphuric acid) are used for making the bed even. All these substances soften at the furnace temperature, and play an important part in the operation.

Bull-dog is a mixture of ferric oxide (Fe_2O_3) and silica obtained by roasting tap (puddling furnace) cinder. This consists of a very basic silicate of ferrous oxide. On roasting, the ferrous oxide (FeO) takes up oxygen, and is converted into ferric oxide (Fe_2O_3), which has very little affinity for silica, and separates from it. A slag—Bulldog slag—rich in silica, runs away.

It is fairly refractory, except in a reducing atmosphere, when the Fe_2O_3 is reduced to FeO, which at once combines with the silica.

With a new bottom, it is usual to introduce a quantity of light wrought-iron scrap (bustling), gradually raise it to a welding heat, and work it into a ball. The oxide produced is spread over the bed. This is repeated every shift of twelve hours, but the bed is repaired after every "heat" by introducing fresh fettling wherever necessary.

The fuel used is a free-burning coal. In furnaces using steam-jet injectors to create a draught, small and inferior coal may be employed, and a great saving effected. The large grate space is necessary to attain the high temperature required in the furnace. The depth of the fire is about 10 inches. When anthracite is employed it is less, while the grate area is increased, and the size of the flue diminished.

[1] It is the slag from reheating furnaces.

The charge generally consists of 5 cwts. of pig iron, with the addition of hammer-scale (Fe_3O_4), etc., as may be required.

The process may be divided into four stages: (1) Melting-down stage. The pig is placed near the fire-bridge, the fire made up, and the damper opened. The manner in which the iron melts, and the temperature, depend on whether grey or white iron is being treated. Grey iron requires a higher temperature than white, and at once becomes very fluid. White iron passes through a pasty state prior to perfect fusion. During this stage, silicon, manganese, and phosphorus are principally removed by oxidation.

(2) The boiling stage. When all is melted, the damper is lowered to somewhat reduce the temperature, and the metal, which slightly stiffens, is thoroughly mixed with the oxides of iron (hammer-scale, mill cinder, etc.) added and produced during the melting-down stage. The oxides of iron in the slag and lining of the furnace rapidly oxidise the remaining silicon and also the carbon in the metal. The temperature of the metal rises, and the whole surface is agitated by the escape of the carbon monoxide generated. Each bubble as it emerges bursts into flame (puddler's candles). During this period, the puddler is continuously employed in rabbling (stirring up) the charge, thoroughly incorporating it with the oxides of iron in the cinder. The boiling gradually subsides, and the metal becomes stiffer and quieter. The carbon has been reduced below 1 per cent., and the third stage supervenes. It is usual in some districts to remove the greater part of the slag at this stage by skimming it off the surface.[1]

(3) The fining stage. During this stage the remainder of the carbon and the manganese are removed, together with some phosphorus. The movements of the metal by carbon monoxide, owing to its pasty state, are sluggish. The metal is rabbled and broken up from time to time, and the damper is raised to thoroughly liquefy the slag. The fluid cinder sinks, and bright points gradually extending over the surface show themselves. These are caused by the burning of the iron, and announce that the metal has "come to nature."

(4) Balling stage. The pasty, spongy mass of malleable iron, now at a full welding heat, is then made into balls, weighing some 70 lbs., by pushing the spongy iron together, and rolling it over the bed of the furnace. As these are made, they are rolled up to the fire-bridge end, and the damper is lowered. The atmosphere of the furnace thereby becoming smoky and reducing, oxidation and waste of the iron is to a large extent prevented. These balls are then removed separately on an iron bogie to the hammer or squeezer, and *shingled* —that is, the particles of malleable iron welded together and the slag squeezed out.

The whole operation takes ordinarily about 1½ hours, divided as follows: 30 to 35 minutes, running down; 10 to 15, boiling; 10 to 20, fining; 20 to 30, balling up and shingling; but may be longer

[1] The agitation produced by the formation and escape of the carbon monoxide may produce a foaming action and flood the slag over the foreplate.

or shorter according to the purity of the metal treated and the temperature and other conditions.

The loss varies from 7 to 20 per cent., according to purity. The greatest loss occurs with siliceous pig, such as is treated in Scotch forges.

The process described above is that followed with grey forge pig, and is technically known as **pig boiling**, the principal decarburising agent being the oxides of iron in the lining and slag, the air only affecting the metal in the running down and balling stages. Some of the chemical changes which take place may be thus expressed—

$$Fe_3O_4 + Si = 2FeO,SiO_2 + Fe$$
$$2Fe_2O_3 + 3Si = 3SiO_2 + 4Fe$$
$$Fe_2O_3 + C + SiO_2 = 2FeO,SiO_2 + CO$$
$$2FeO,SiO_2 + O = Fe_2O_3 + 2SiO_2$$

The silica formed is fluxed off by oxide of iron, of which there is always large excess, and the carbon is removed as carbon monoxide. Manganese is oxidised to MnO, which replaces FeO in the slags, rendering them very fluid. The phosphorus is removed by oxidation, and passes into the slag as phosphate of iron. It is possible that to some extent it liquates into the slag as phosphide of iron, and is subsequently oxidised.

Dry Puddling, as it is called, as now conducted, differs but little from the pig-boiling process, save that white or refined iron is the metal operated on, and the slag is removed so as to keep the bottom "dry." In consequence the action is less vigorous, and the amount of slag less. The temperature is lower throughout until the balling stage is reached, the metal never becoming perfectly fluid, and being continuously rabbled. The decarburisation is mainly effected by the air passing through the furnace. Formerly it was conducted on a sand bottom. Owing to the nature of the iron employed, there is, of course, less loss. It is still practised in a few forges making "Best Yorkshire Iron."

Tap-Cinder, as the slag from puddling is called, consists of basic silicate of iron, with smaller quantities of lime, alumina, oxide of manganese, and phosphoric acid. Sulphur, probably as iron or manganese sulphide, is also present. It is a black mass, with a dull granular fracture. It may be represented by the formula $2FeO,SiO_2$. In the puddling process it acts as a carrier of oxygen to the impurities in the pig, the ferrous oxide it contains being oxidised and subsequently reduced. It contains from 40 to 60 per cent. of iron, and is tapped from the furnace into rectangular iron wagons. An inferior class of pig iron, known as *cinder pig*, was made from it by smelting in the blast furnace. It is now smelted for the production of "basic" pig rich in phosphorus.

The sulphur in pig iron is not removed by oxidation either in puddling or finery methods. A considerable portion, however, does pass into the slag, probably by liquation. Its removal is facilitated by any cause which tends to prolong the operation or to render the slag fluid. For this reason, manganese in iron, by prolonging the fining stage and the effect of the oxide formed in giving greater fluidity to the slag, promotes the elimination of this element. It appears to pass

out during the whole operation Various " physics " are employed. **Schaffhautl's** powder is a mixture of oxide of manganese, salt and clay. **Scheerer's** consists of calcium chloride and salt, and soda-ash.

Improvements in Puddling.—Besides the introduction of steam-jet injectors for forcing the draught, various contrivances to diminish labour and save fuel have been introduced.

Mechanical rabbles of various types have been used, but the finishing and balling of the charge had always to be done by hand.

Mechanical furnaces of various types in which the working of the charge is effected by movement of the furnace, bed or chamber have been introduced.

The Roe furnace is a gas fired regenerative furnace with a bed oscillating on a horizontal axis. It takes a charge of some four tons and the yield is said to be 20 per cent. higher than the pig charge due to reduction of iron from the fettling. The operation occupies about 1½ hrs.

Dank's furnace was a rotary furnace. It is no longer used.

In Pernot's furnace the hearth revolved in a plane slightly inclined to the horizontal.

FIG. 92.—Photo-micrograph showing slag inclusions in wrought iron.

The Hibbard furnace is an oil-fired cylindrical furnace, with a magnesite lining capable of oscillating or rotating. A longitudinal ridge runs the length of the furnace, over which the iron and slag are thrown by the oscillation of the furnace and thoroughly mixed. When treatment is complete and the ball has collected the furnace is revolved and finally the cylindrical bloom is dropped through a door extending along the side opposite the ridge. The bloom weighing about 1500 lbs. drops on to a belt conveyor and is transferred to a squeezer for shingling.

The waste heat from puddling furnaces is generally used for raising steam.

Shingling and Rolling.—The " balls " taken from the puddling furnace consist of a sponge of malleable iron saturated with slag. The consolidation and welding together of the particles, and the expulsion of the slag, are technically known as *shingling*. The freedom of the wrought iron from slag will depend upon the efficiency with which the operation is conducted. (See Fig. 92.) This process takes the form of hammering or squeezing.

The *crocodile squeezer* is shown in Fig. 93. It consists of two jaws, the lower of which is fixed and forms the anvil, while the upper opens and closes upon it, actuated by the revolution of the crank. The ball is placed between the open jaws and turned over and moved toward

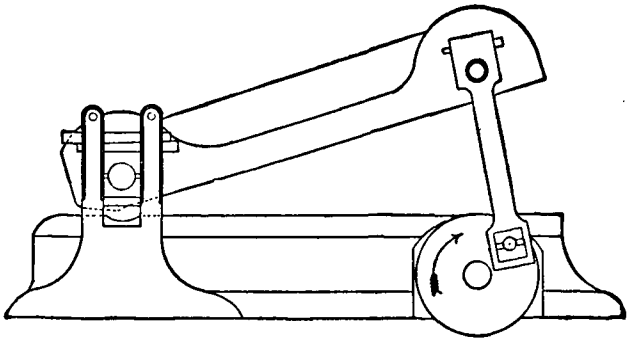


FIG. 93.

the back part of the jaw as the mass gets reduced in bulk and consolidated by the expulsion of slag, which flows out over the sides of the anvil. Many other forms of squeezer are also employed.

The *helve* or *shingling hammer* is shown in Fig. 94. The head, weighing about 4 to 10 tons, is raised (by the cams on the wheel revolving in front) from 15 to 20 inches, and allowed to fall on the ball

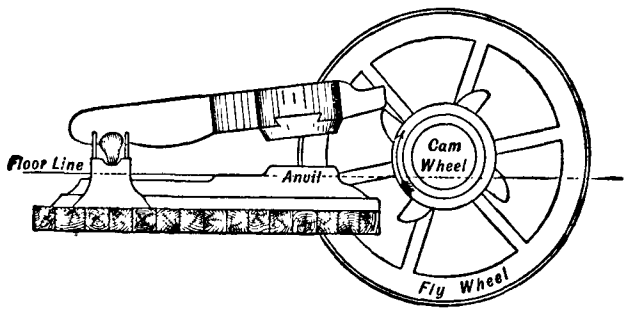


FIG. 94.

placed on the anvil-block. The number of blows is from 60 to 100 per minute. In belly-helves, the cams act on the lever at a point midway between the head and the fulcrum.

The objection to the helve is that the weight of the blow is the same at the beginning of the operation, when the ball is tender, as when it has become more solid.

Steam-hammers are now almost universally employed. They consist of an inverted upright steam cylinder, to the piston rod of which the head or "tup" is attached. This slides between vertical

guides on the standards which support the cylinder. The admission of steam to the cylinder is controlled by a handle which works the valves through a system of levers. In double-acting hammers, steam is admitted below the piston to raise the head, and also above the piston to force it down and increase the weight of the blow. In single-acting hammers, steam is only admitted below the piston to raise the tup, which then falls by its own weight. The larger hammers for forging purposes are of the former type.

The legs of the shingler are encased in iron guards, and the face protected by an iron mask, to protect him from slag, which flies about in all directions. The ball is placed on the anvil, and receives at first a few light blows. This is effected by admitting a little steam under the piston as the head falls, thus forming a cushion and diminishing the force of the blow. The weight of the blow is gradually increased, the ball being turned at each stroke, until it has been hammered into a rectangular "bloom," and the slag thoroughly expelled. The bloom is still hot enough to be rolled out into bars, and is dragged over the iron plates of the floor to the "puddle rolls," or forge train.

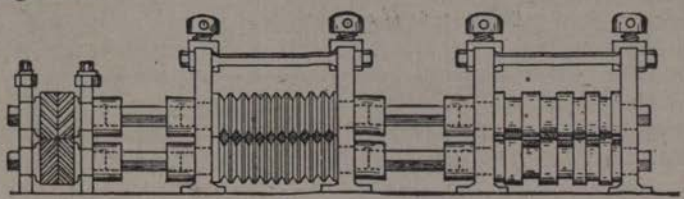


FIG. 95.

These consist, as shown in Fig. 95, of two pairs of iron rolls, 15 to 18 inches in diameter, mounted in suitable housings, the lower one being driven directly from a steam-engine. One pair of rolls, known as the *roughing* or *cogging* rolls, has a series of gothic, or V-grooves, of diminishing size; and the other, known as the *finishing* rolls, a series of rectangular grooves.

The surface of the grooves in the roughing roll is notched or chisel-cut, to enable them to grip the bloom and drag it through. It is first pushed endwise into the widest of the grooves in the roughing rolls. As it leaves the rolls on the other side, it is seized and passed back by resting it on the top of the upper roll, which, by its revolution, carries it forward. It is then passed through the next groove, and this is repeated until it has been reduced to the required size. It afterwards makes one or more passes through the rectangular grooves of the finishing roll, and is thus reduced to a flat bar, which is dragged aside and allowed to cool. It then constitutes "puddle bar," on the weight of which the puddler is paid. The fracture is bright and crystalline, or granular. The puddle rolls make about seventy revolutions per minute. The surface of the rolls and the bearings are kept cool by jets of water.

Puddled bar is never homogeneous, and includes particles of slag not expelled during shingling.

Crown or Merchant iron is produced by cutting the puddle bar into suitable lengths and arranging them in a "bundle," "pile," or "faggot," which, if large, is tied by iron wire. The size of the pile depends on the size of the bars, etc., to be produced. It is raised to a full welding heat in the *reheating* or *mill furnace*, which somewhat resembles a puddling furnace, but is without a flue-bridge.

Reheating furnaces working with gas, and provided with regenerators, are now commonly employed.

When fully hot, the piles are withdrawn, and the bars welded together under the hammer or in a blooming-mill, the pile being afterwards reduced to a size suitable for rolling.

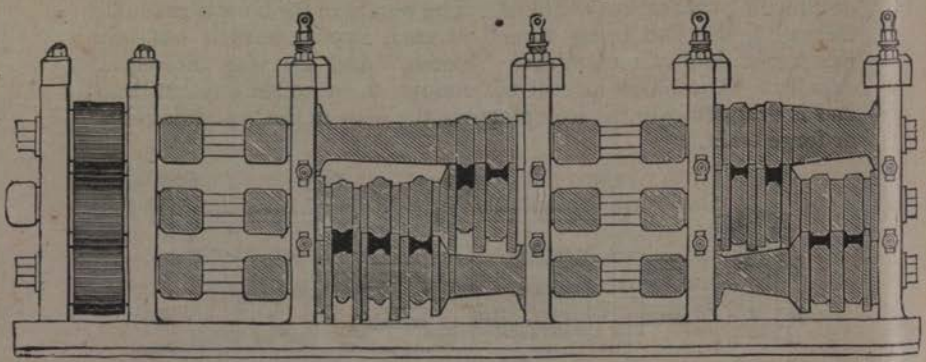


FIG. 96.—Three-high rail mill.

It then passes to the *mill train*, which consists, as before, of two sets of rolls—roughing and finishing. The bloom is cogged down to the required extent in the roughing rolls, and then passes to the finishing rolls to be converted into rounds, squares, angles, or any other form (section) required. The finishing train has chilled iron rolls, and the grooves are turned with great accuracy. Sometimes, instead of at once finishing, the billet, after rolling down, is cut up, and piled, reheated, and again rolled. It then forms No. 3, or best iron, while, if this is again piled and reheated, best best iron results.

The oxide of iron formed in the reheating combines with the sand of which the furnace-bed is made and forms a slag, which flows out of an opening in the flue towards which the bed inclines. It is known as *fine cinder* and *mill-furnace* slag. It consists of ferrous silicate, with a large excess of oxide of iron, and has a lustrous crystalline fracture.

Light work is guided into the rolls by various devices, and is consequently known as *guide iron*.

In rolling plates, plain rolls are employed. The billet is passed in one direction until the required width has been obtained, and then turned at right-angles and rolled down to the desired thickness.

The distance between the rolls is regulated by setting-down screws, which act on the top bearing of the upper roll; and in rolling plates, the distance between them is diminished at each pass, both ends being set down by the same amount. The weight of the upper roll is counterbalanced. The roughing rolls are of grain iron, but the finishing rolls are chilled on the surface. Heavy plate mills are either provided with reversing gear, or are driven by reversing engines, so as to obviate passing the work back over the top roll.

Thin sheets are rolled by doubling and passing the compound sheet through the rolls. Sometimes as many as sixteen thicknesses are being rolled at one time (see Tin Plate).[1]

For light work, to save the time of passing it from the back to the front, and the consequent cooling down which takes place, three-high rolls are employed. The middle one is driven from the engine, and the others geared with it. The work having passed through the lower pair is returned through the upper. Rolling takes place in both directions.

Three-high mills for heavy work are provided with rising and falling tables, which receive the work as it leaves the rolls, and raise or lower it as required. Rolls for rolling finished iron vary from 8 inches to 38 inches in diameter.

The rolling of malleable iron, by welding together and elongating the particles of iron, develops a fibrous structure, which is more pronounced the greater the number of times it is piled and reheated. This treatment also renders the metal more uniform in character.

COMPOSITION OF MALLEABLE IRON.

Carbon	0·1 to 0·3	Sulphur	0·02 to 0·15
Silicon	traces ,, 0·1	Manganese	traces ,, 0·25
Phosphorus	0·04 ,, 0·2	Iron	99·1 ,, 99·8

Burnt Iron.—When iron is exposed at a very high temperature to an oxidising atmosphere, it loses its malleability and is known as *burnt* iron. Probably this is due to the formation of a suboxide of iron in the metal.

Brands of Merchant Iron.— (Crown), common iron, or merchant bar (puddle bar, once piled and reheated). Best, twice piled and reheated. Best best, three times piled and re-heated. Treble best, four times piled and reheated.

Scrap bar is made by heating scrap to a welding heat in a " balling " furnace. This is similar to a puddling furnace. The slag is known as ball furnace slag. The quality of the iron varies.

[1] Continuous mills, rolling down from billet or ingot to the required thickness are rapidly coming into use. In the thinner sections the metal has cooled down and in the later passes is " cold " rolled.

Such mills are of great length. The new mills at Ebbw Vale and Shotton are of this type. Continuous rolling maintains an even temperature at the roll surface, avoiding changes of volume and shape due to expansion. This ensures uniformity of product, especially of the surface.

CHAPTER XI

STEEL

THE designation of steel was formerly confined to those varieties of carburised iron which could be hardened by heating to redness and plunging in cold water.

The introduction of the Bessemer process marked a new era. The soft metal produced by this process, though containing little carbon, lacks the fibrous character associated with wrought iron, and partakes more or less of the character of steel. Those varieties possessing more than 0·3 per cent. of carbon sensibly harden when treated in the same manner as steel, but with less carbon this is not the case. Other processes producing similar soft metal sprang up, and the term *steel* has come to include a great variety of materials, having widely different properties. Some are softer even than wrought iron.

Straight Carbon Steel.—Since the hardening property is dependent on the amount of carbon it contains, a classification based on the percentage of that element is the most convenient, steel containing less than 0·5 per cent. being classed as *mild* steel. Steel proper contains from 0·5 to 1·5 or 1·7 per cent. of carbon. The different nature of these metals may be shown by the use of such titles as Bessemer, Siemens's or open-hearth steel. Some of these contain as little as 0·08 per cent. of carbon, less than is often present in wrought iron. They differ from that metal in being devoid of fibre, more homogeneous, and, unlike it, *are obtained in a state of fusion*, and cast in ingots. The term *ingot iron* would be more applicable than *steel.*

The fracture of steel becomes finer the larger the proportion of carbon present, but is affected by such treatment as hammering cold. Steel of hard temper[1] breaks with a clear, uniform, grey, finely granular fracture. After hardening, the colour is somewhat whiter.

It is very malleable, but requires working more carefully and at a lower temperature than wrought iron. Steel containing less than 1·25 per cent. of carbon can be welded. A lower temperature must be employed than for malleable iron, or the steel will be burnt. To render the surfaces clean at the lower heat, borax mixed with about one-tenth of its weight of sal ammoniac is employed to dissolve the scale.

The specific gravity varies from 7·624 to 7·813 in the unhardened state, to 7·55 to 7·75 in the hardened condition, showing that expansion occurs in the process.

[1] The term " temper " applies only to the proportion of carbon present.

The melting-point varies with the proportion of carbon. The softest melts a little below 1500° C. The hardest at about 1350°.

The *tenacity* varies from 22 tons in mild steel to upwards of 70 tons in steel of hard temper. Its *elasticity* exceeds that of wrought iron, while its *ductility* may equal the best qualities of that substance. The mild varieties suffer an elongation and diminution in area, when subjected to a stretching force, greater than does wrought iron. The elongation of the harder varieties is much less, but the elastic limit is high.

Hardening and Tempering.—The extent to which hardening occurs depends on the proportion of carbon in the metal, and the rate and manner of cooling from redness.[1]

Thus, quenching in mercury or other good conductor of heat produces greater hardness and brittleness than quenching in water, while quenching in oil (oil hardening) produces a degree of hardness, without brittleness (owing to the slower cooling action of the oil), whereby the elasticity, tenacity, and toughness of the steel are increased. Springs and gun tubes are treated in this way.

Hardened steel may be rendered soft by heating for a prolonged period at a high temperature, and allowing it to cool down very slowly. This is called annealing.

When steel, rendered brittle by hardening, is heated at temperatures below redness, the hardness is partially removed, and it recovers to some extent its elasticity; the higher the temperature attained, the softer and tougher will the hardened metal become. This operation is known as *letting down* or *tempering*. If the surface of the hard steel be polished, on gradually heating in air, it becomes first a pale straw colour, and afterwards dark straw, golden yellow, brown, brown with purple spots, purple, violet, and blue, as the heating proceeds. These tints serve to mark the temperature attained, and, in tempering tools and cutting instruments, indicate to the workman the point at which they should be cooled off. The colours are probably due to thin films of oxide formed on the surface. The hardness which they indicate depends on the nature of the steel. Below is a table giving the temperatures indicated, and some articles let down to the respective tints.[2]

220° C. light straw: lancets, razors, and surgical instruments.
230° C. dark straw: surgical instruments, razors.
245° C. full yellow: penknives, wood tools, taps, dies.
255° C. brown: cold chisels, hatchets, etc.
265° C. brown with purple spots: axes, plane-irons, pocket-knives.
275° C. purple: table-knives, large shears.
295° C. violet: swords, watch-springs, augers.
320° C. full blue: hand and pit saws, etc.

The changes in the hardness and physical properties of steel are due to changes

[1] Strictly speaking from above the Ar 1 point. See p. 373.
[2] This should be read in conjunction with the table on p. 183.

occurring in the iron itself and the manner in which the carbon is present in the metal.

When pure iron is heated to 900° C. it changes its molecular structure and becomes another kind of iron, much in the same way as phosphorus changes. On heating to 234° C. yellow phosphorus—waxy, very inflammable, and poisonous—changes to the amorphous, red powder, fire-safe, non-poisonous variety. In the same way this new variety of iron has independent properties. To distinguish the two, ordinary iron, *i.e.* untreated at ordinary temperatures—the form it assumes when allowed to cool without quenching—is known as α (alpha) iron, the form into which it passes when heated, and which under certain conditions may be made permanent, is known as γ (gamma) iron.

Gamma iron when hot, in the solid state dissolves carbide of iron readily, that is, the carbide diffuses into it and becomes uniformly distributed as if in solution; alpha iron does not dissolve the carbide, and when the change from γ to α iron occurs, as the metal cools the carbide separates. The change from α to γ iron occurs in pure iron at about 900° C., but the temperature at which the change takes place is largely influenced by certain elements and depends on the amount of the element present.

Thus the gradual increase in the percentage of carbon lowers the temperature of the change point until, with a proportion of 0·89 per cent.—corresponding to 13·2 per cent. of carbide (see p. 373)—the lowest temperature, about 690° C., is reached. Carbon is not capable of lowering the temperature of the change point below this. Some other elements—*e.g.* chromium, manganese—do.

The changes of γ to α and α to γ are reversed on heating and cooling at about the same temperature. The less the amount of carbon present, the nearer the change point is to 900° C.

Iron containing carbon heated above the change point will hold its carbide in solution, but on cooling slowly without quenching the carbide will separate as the metal cools below the change point. If quenched above the change point the carbide will remain dissolved (its separation being prevented by the rigid molecular condition of the cold metal), and influences its hardness and other properties in proportion to the amount present. In cooling, the passage of the change point is marked by a liberation of heat. In pure iron the amount liberated is small, being the energy given out by the metal in changing its molecular character. It may be detected by delicate instruments. See p. 350.

In carburised iron—steel—the amount given out increases with the amount of carbon present up to 0·89 per cent. In steels containing more than 0·6 per cent. carbon this can be made visible. If a strip of such steel be heated to redness and held to cool in a shady place it will be observed that the metal will become nearly black-hot and then suddenly brighten up visibly, after which it will cool in a normal manner.

Similar liberations of heat occur with less carbon, but may not be sufficient to produce a visible effect.

The phenomenon of self-reheating is known as "**recalescence.**" The temperature at which it occurs marks the point at which changes in the iron itself are taking place and the temperature at which the carbide separates. The separation of the carbide is responsible for the larger amount of heat liberated from more highly carburised steel.

On heating, a quantity of heat equal to that evolved in cooling is taken up by the metal and produces an arrestment or retardation of the heating.

Steel heated for a period above the recalescence point and quenched will be hardened. If quenched below that point it will not be hardened.

Other substances beside carbon influence the temperature at which recalescence takes place, and thus the hardening temperature.

Manganese in sufficient quantity lowers it below the ordinary temperature, and the metal is permanently hard.

Other metals behave in the same way. It is upon these effects that the self-hardening property of alloy tool steels depends.

The changes occurring in steel by quenching under different conditions are indicated in Fig. 97.

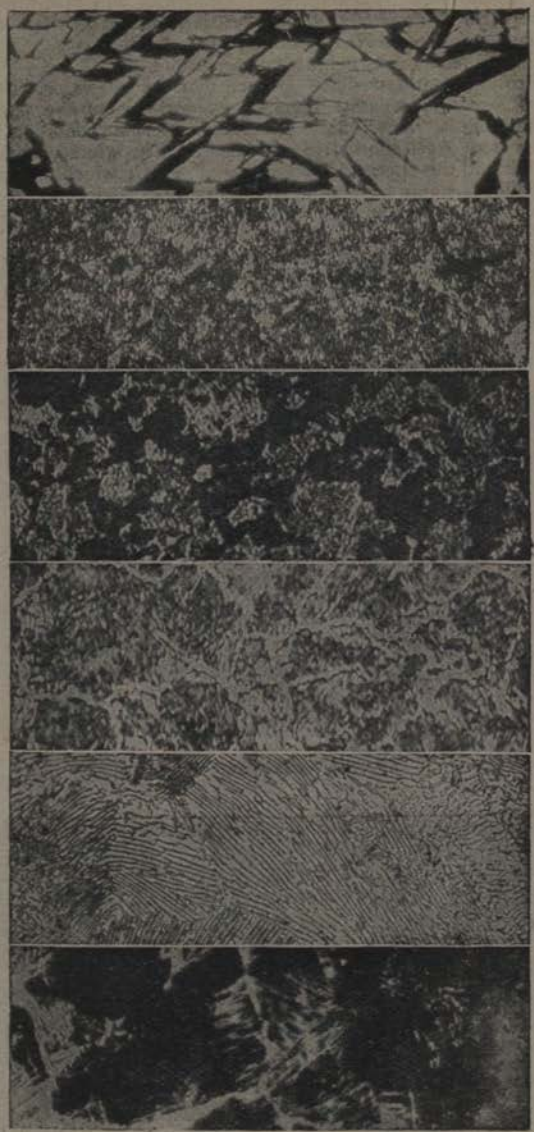


FIG. 97.—Changes produced in structure of steel by heat treatment.

A. The metal contains 1·5 per cent. carbon, and was quenched from 1100° C. in ice-cold water. The carbide is uniformly diffused through the metal. The condition is known as "austenitic." The metal is softer and tougher than B.

B. The condition is "martensitic." The metal was quenched above 900° C. and is in its hardest and most brittle form. The white specks represent carbide not redissolved by the metal.
The metal resumes its magnetic character at 768° C.

C. is a condition intermediate between martensite and pearlite. The carbide has begun to separate but has assumed no definite arrangement. The condition is "troostitic." It is the most elastic condition of steel.

D. is the same steel allowed to cool slowly. The white material enclosing the grains is the excess of "cementite," Fe_3C, which separated during the cooling, leaving a material containing 0·89 per cent. carbon. This is the maximum amount that can be retained in solution at the point of recalescence.

E. shows the laminated internal structure of the grains highly magnified (pearlite). It consists of alternate laminæ of α iron and cementite. The steel is in its softest condition.

F. shows the structure of steel when much overheated.

FIG. 98.—Steel much overheated.

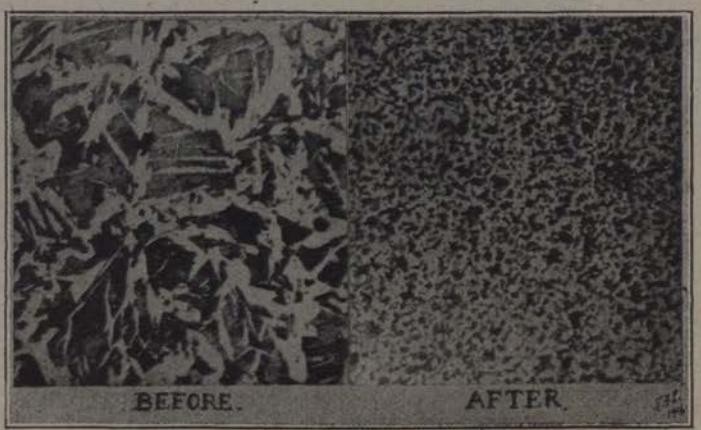


FIG. 99.—Micrograph of steel forging, showing effect of heat treatment.

Austenite, martensite, troostite, sorbite,[1] and pearlite are the structures that may be obtained by quenching suitable steels at different temperatures or by heat-treating them after quenching.

The heat treatment of steel for different purposes is carried out to develop a suitable condition by a careful control of the conditions of heating and cooling.

Modern methods of hardening are much more exact. In Brayshaw's furnace the articles are heated in a bath of fused salts to obtain uniformity. Pyrometers are used to control the temperature.

VARIOUS QUALITIES OF STEEL.

Description.	Percentage of carbon.	Character and uses.
Mild steel	0·1 to 0·25 (0·2 ,, 0·4 Mn)	Soft malleable metal for rivets and plates.
	0·3 ,, 0·6	Harder and stronger for rails, forgings, etc.
	0·4 ,, 0·5	For tyres and castings.[2]
	0·5 ,, 0·6	For hard wire, for guide ropes, springs, etc.
Die temper	0·75	Is tough, capable of resisting great pressure, is very easily welded. Used for stamping and pressing dies, welding steel for axes, plane-irons, etc.
Sett temper	0·825	Is hard, tough, strong, capable of resisting sudden and great shocks, blows, etc. Used for cold setts, minting dies,[3] and smiths' tools; easily welded.
Chisel temper	1·0	Is easily forged; hard even when let down low, and sufficiently tough to withstand blows; is weldable. Used for cold chisels, miners' drills, large punches, etc.
Punch temper	1·125	Is a hard, fine-grained metal. Takes and maintains a good cutting edge; is more difficult to work, but welds with great care; used for circular cutters, taps, rimers, large turning tools and drills, screwing dies, etc.
Turning-tool temper	1·25	Is unweldable, and must be carefully treated in forging, hardening, and tempering; is generally useful for turning, planing, and slotting tools, drills, small cutters, taps, saw-files, etc.
Small-tool temper	1·375	
Razor temper	1·5 and upwards.	This and the last variety are unsuited for any purpose where sudden variation in pressure, etc., occurs. Can only be dealt with by a skilful workman, and if at all over-heated, is spoilt. Used for razors, surgical instruments, small tools, etc.
High speed steels	0·5 to 0·7	These contain chromium, 2·5 to 4·5 per cent.; tungsten, 9 to 18 per cent. Sometimes vanadium, molybdenum, and other elements are present. They are self-hardening. They are also used for dies.

The harder varieties of steel occupy an intermediate position, between malleable iron, on the one hand, and cast iron on the other. The comparison ends with the carbon contents of the metal. In all

[1] Sorbite is a non-laminated (granular) structure intermediate between troosite and pearlite, produced by quenching during recalescence.

[2] In modern tyres this is often exceeded, 0·65 being reached.

[3] Minting dies now contain up to 0·89 per cent. carbon.

tool steels, save special kinds to be noted hereafter, the other elements present in cast iron are found only in minute quantities. They exist in appreciable amounts in the metal obtained from all processes in which steel is made direct from cast iron.

Steel-making.—The methods of producing steel may be classed as follows :—

1. *Direct methods*—
   (*a*) From iron ores.—Catalan and analogous processes.
   (*b*) From cast iron.—Puddled steel.
2. *Indirect methods*—
   (*a*) By the carburisation of malleable iron in an unfused state.—Cementation and case-hardening processes.
   (*b*) By carburisation of molten malleable iron.
      (1) Fusion of bar iron with carbon in crucibles.—Cast crucible steel and Wootz processes.
      (2) The carburisation of molten iron obtained by complete or partial decarburisation of pig iron. Bessemer and open-hearth processes.

Steel in the Catalan Forge.—Excellent steel of middle temper can be made in open hearths of this type, by giving the tuyère less inclination, so that the blast does not play so directly on the accumulating mass of metal, and removing the slag more frequently than in making malleable iron.

In making *steel* in these hearths, less small ore is added, so that the slag is less basic, and less blast is employed. By these means the reduction is somewhat prolonged, affording opportunity for carburisation by decomposition of carbon monoxide by the spongy iron, while the direction of the tuyère and the removal of the slag prevent decarburisation by the oxide of iron it contains, and by the air. The presence of manganese in the ore is also favourable to the production of steel. Its oxide gives greater fluidity to the slag, and is less energetic as a decarburising agent.

Puddled Steel.—Steel can be made in the puddling furnace by arresting the process before decarburisation is complete, sufficient carbon being left to constitute steel. White pig irons containing manganese and free from sulphur are best adapted for the purpose.

Cementation Process.—This is by far the most[1] important method of producing steel for cutting-instruments, *i.e.* steels of hard temper. As previously noted, when iron is heated in contact with carbon, carbon monoxide, or compounds of carbon and hydrogen (hydrocarbons), to a high temperature, carbon is taken up by the iron. This is the basis of the process by which all the best qualities of carbon steel for cutlery, springs, etc., are produced. The superiority of the method is due to the fact that practically pure iron is employed for the purpose. Swedish bar iron, made in the Swedish-Lancashire hearth under charcoal, from charcoal pig, is the material usually operated on, so that such steels practically consist solely of iron and

[1] Since the introduction of electric furnaces the supremacy of cementation is challenged.

carbon. The bars employed are about 10 feet long, 3 inches wide, and $\frac{5}{8}$ inch thick. Hammered bars are preferred. Basic steel bars are also sometimes employed.

The converting furnace is shown in Fig. 100. The furnace proper consists of a rectangular arched chamber, A, of fire-brick. This communicates by the chimneys B B, three on each side, with the hovel C about 40 feet high, which serves as a chimney and diminishes the loss of heat by radiation. It gives the furnace the appearance of an ordinary glass furnace. A narrow fireplace, 12 to 15 inches in width, runs down the middle, with a firing door at either end. On each side of the fireplace is a *trough* or *pot*, D, for the reception of the bars of

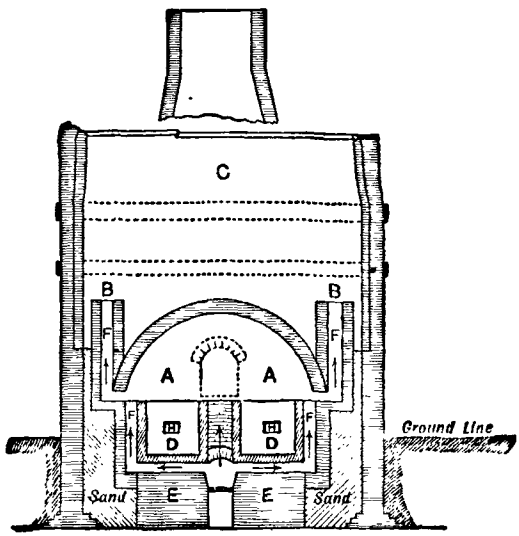


FIG. 100.

iron. They are made of firestones, open at the top, and rest on the benches E E on brick bearers, which divide the space below the pots into a number of flues, F. These are continued up the sides and ends of the pot; the space above the fire is similarly divided, in order that the boxes may be heated as uniformly as possible.

The pots are from 10 to 15 feet long, $3\frac{1}{2}$ to 4 wide and deep. In the end of each is a small opening, H, known as the tap-hole. This is opposite a similar opening in the outer wall, and through it the *tap* or trial bars are withdrawn. From the appearance of the fracture of these, the progress of the operation is judged. Manholes are provided for the purposes of charging and discharging the pots, and are closely bricked up during the conversion.

The pots are charged by first spreading a layer of charcoal nubs (about as large as peas or beans) over the bottom. On this a layer of

bars, about half an inch apart, is placed. A second layer of charcoal, followed by bars, is then put in, and so on, until the pots are full, finishing off with charcoal. The charge is covered with "wheel-swarf."

This is the refuse from under the grindstones, and consists of particles of oxidised (rusted) iron and sand. At the high temperature of the furnace, this frits and forms a rough glass, which hermetically seals the pots and excludes air.

The manholes are bricked up and carefully luted, as also is the space round the trial-bars. A coal fire is then made and the temperature gradually raised. In about 24 hours the pots are at a dull red heat, and in about 50 hours or more, the bright red or yellow heat (1100 to 1200° C.) required for conversion is attained. This is steadily maintained for a period of from 4 to 8 or 10 days, depending on the degree of carburisation required. For springs, saws, etc., 4 or 5 days suffice. For shear steel, 5 or 6 days; double shear, 7 to 8 days; and tool steel, 10 days or more. The progress is judged by the appearance of the fracture of the trial bars, a distinct layer of steel of greater or less depth is formed, enclosing a "sap" of unaltered iron, but there is no sharp line of demarcation. When the operation is completed, the fires are allowed to burn out, and the furnace to cool very gradually. This occupies about a week, and the pots are then discharged. The bars present a blistered or warty appearance, and a laminated structure and are hence known as *blister steel.*

These blisters are evidently formed by the efforts of gas to escape from the interior of the bar while in a soft state. The gas is formed by the action of the carbon on particles of slag, containing oxide of iron, enclosed in the iron.

The bars are brittle, and are sorted out by breaking with a hand hammer on a block, and examining the fracture. No. 1, "spring temper," shows a comparatively thin skin of steel enveloping unaltered iron. In No. 4, "double shear heat," the proportions of steel and iron are about equal. In No. 6, "melting heat," the "sap" has disappeared, and the conversion has extended through the bar. The carburisation is probably due to the decomposition, by the iron, of carbon monoxide produced from the oxygen in the small amount of air retained in the pot and in the pores of the carbon (see page 77). As before noted, iron at redness is easily permeated by gases, and thus carbon is carried into the interior of the bar. The amount of carbon taken up varies with the time and temperature up to 1·5 per cent. or even more.

Blister Steel is brittle, crystalline, and lacks homogeneity. For most purposes it is either tilted or melted.

Shear Steel.—The blister bar is cut up, plated,[1] faggoted, reheated, and welded, and then either drawn out under the hammer or rolled, in a manner resembling the treatment of iron, to obtain greater uniformity. If, after welding, the metal is doubled on itself, reheated,

[1] Hammered flat.

and again welded, it forms double shear steel. By this treatment the percentage of carbon is very slightly reduced by oxidation, and only the milder tempers with less than 1·125 per cent. of carbon can be satisfactorily welded. The pile is frequently coated with clay wash and borax, to protect it from oxidation and facilitate welding. Tilted steel has lost the laminated appearance of blister steel and is more uniform in character and composition.

Cast Crucible Steel.—Steel produced as above must necessarily be far from homogeneous. In 1740, Huntsman introduced the practice of melting down the blister steel in crucibles, pouring it into ingot moulds, and working the ingots into bars, etc. The fusion ensures uniformity of character and composition, hence the term *homogeneous* metal or steel applied to it. Its commoner designation is *crucible cast steel*.[1]

The steel-melting holes or fires (see Fig. 101) are simple wind furnaces of oval section, lined with ganister. They are placed below the floor level for convenience of handling the pots. Each fire has a separate flue, which is continued down behind the furnace, and opens into the ash-pit. The draught is regulated by the insertion or removal of a brick in this opening. The crucibles, which are dried on shelves round the melting-house, are from 16 to 19 inches high and 6 to 8 inches in diameter at the mouth. Each fire takes two pots. Before placing them in the furnaces they are annealed in a coke stove or gas furnace for some hours, gradually attaining a dull red heat. The blister steel is cropped up into small pieces, and the charge is introduced into the heated crucibles by means of an iron funnel. The pots generally last about three melts, the weight of the charge being less each time. Thus a first charge of 50 lbs. will be followed by charges of 45 and 40 lbs. respectively for the second and third heats.

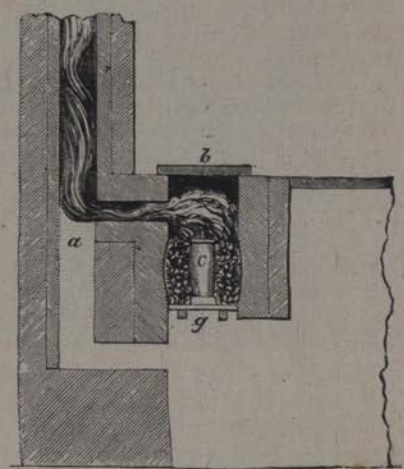


FIG. 101.

The charge having been introduced, the lid is put on, the fire is made up with hard, free-burning coke, and the furnace closed. The first fire burns off in about forty-five minutes, and is followed by a second and third firing. The amount of fuel added in the third fire is judged from the amount of metal remaining unmelted, to ascertain which, the workman pokes an iron bar into the pots and gives direc-

[1] Melting is now done in high-frequency induction furnaces. See p. 203.

tions accordingly, in order that all the crucibles may be ready at one time. The crucibles are lifted from the fires, for teeming, by grasping them round the belly with tongs having bent jaws, which encircle the pots. The first melt occupies from 4 to 5 hours.

The slag is removed before teeming by moving a knob of slag (mop), attached to an iron bar, over the surface of the metal, by which means the slag is cooled, collects on the mop, and is removed.

Small ingots are run from a single pot. For larger ones the pots are *doubled*, that is, the contents of two pots are transferred to one before teeming, while for still larger ones the metal from the crucibles is transferred to a ladle similar to that described (see p. 205), or arrangements must be made to keep up a constant stream of metal into the mould.

The ingot moulds are of cast iron, and made in two parts. While casting they are held together by an iron ring. The moulds are warmed and reeked, that is, coated with lamp-black, by smoking them with the flame of burning tar. Sometimes a wash of clay is applied. This treatment prevents the ingots from sticking. In pouring, the hot stream of metal should not touch the sides. A fireclay hollow plug, known as a core or dozzle, is now put in the mouth of the ingot mould and the metal poured through it.

The pots, if in good condition, are returned, after detaching clinker, etc., to the fires, ready for the next charge. If allowed to cool, they cannot be reheated without cracking. In melting blister steel, it is usual to add a small quantity of black oxide of manganese, which is partly reduced, and manganese passes into the metal.

Direct Cast Crucible Steel.—In casting large ingots of crucible steel, bar iron or puddled steel is employed instead of blister steel, charcoal, spiegel, and ferro-manganese being added to carburise the metal to the desired degree. Ingots 40 tons in weight have been cast.

Fig. 102 shows a regenerative crucible furnace for steel melting. They take from 8 to 24 pots in a double line. The roof is in several sections, which can be removed as required for charging or teeming purposes. Some furnaces of this type are provided with a movable bottom, which can be elevated, by a hydraulic ram, to the floor level, with all the pots standing on it.

Plumbago pots, having a larger capacity than those described, are also employed They are more durable than ordinary white or black pots (*i.e.* clay, or a mixture of clay and coke-dust), and with care will bear reheating after cooling. They last from 9 to 11 melts.

Honeycombing.—Steels, especially those of mild temper (below 0·5 per cent. of carbon), are liable to boil up in the mould after teeming. This is due to the disengagement of dissolved gases, mainly H, N, and CO, which are given off as the metal cools. The bubbles of gas cause the metal to be honeycombed and vesicular. With a view to prevent boiling up, a stopper, which fits loosely, is put on the top of the metal, and a little sand thrown on and round it to keep it down; or sand is thrown on the top of the metal and an iron cover is put on and held down by wedges passing through eyes on the top of the mould.[1]

[1] This treatment is only possible with Bessemer and other large ingots.

The upper part is most affected, the gases from the lower part rising, in consequence of the metal at the bottom remaining fluid for a longer time. The presence of the stoppers prevents the top from cooling so rapidly.

Piping.—Steel of harder temper (above 0·7 per cent. of carbon) settles down in the mould, forming a funnel-shaped cavity or pipe. The ingot is *topped* by breaking off the unsound part before working. Both these evils may be largely mitigated by careful melting and teeming at the proper temperature.

Dead-melting.—If not heated a sufficient length of time, the metal is not "killed," and will teem "fiery"—throwing off sparks—and be honeycombed. If "dead-melted," this does not occur, but if left too long in the fires it will teem "dead," and be weak and brittle.

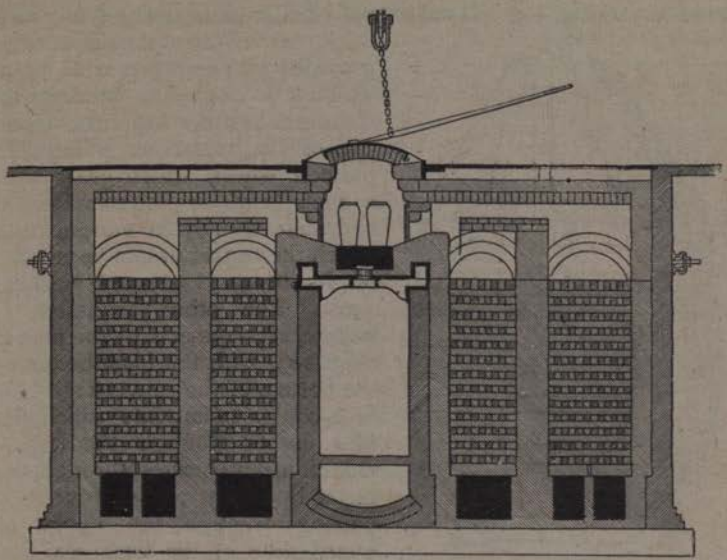


FIG. 102.—Regenerative crucible furnace.

Case-hardening.—The surfaces of wrought iron and mild steel articles subject to wear, are often superficially hardened by packing them in iron boxes, with parings of horns and hoofs, leather scrap, bone-dust, and charcoal, and heating to full redness. The depth of the hardening depends on the length of time they are heated. Small articles are case-hardened by heating them to redness and sprinkling with or rubbing them in powdered yellow prussiate of potash (potassium ferro-cyanide). The carburisation is effected by the cyanogen (*CN*) compounds. The articles require quenching and heat treatment.

Production of Steel from Pig Iron without previous conversion into malleable iron. These processes involve the removal from the pig of the silicon, sulphur, and phosphorus, and the reduction of the amount of carbon to the quantity required to convert the metal into steel. It is found more satisfactory, however, to completely remove carbon as well, and recarburise by the addition of carbon in some form or other, generally as spiegeleisen or ferro-manganese; but anthracite, gas carbon, and other substances are also employed (Darby process).

Bessemer Process.—In the Bessemer process the impurities are burnt out of the pig by blowing air through the molten metal. Referring to p. 166, it will be seen that under proper temperature conditions all the impurities, except sulphur, will practically be oxidised before the iron, so that by stopping the blast at the right moment, and adding a quantity of spiegeleisen or other carbon-bearing material, sufficient carbon may be introduced to produce steel of the desired temper.

The process is generally conducted in a vessel or converter of the form shown in Fig. 103. It consists of a boiler-plate casing $\frac{3}{4}$ to 1 inch thick, carried on a cast-iron ring, provided with trunnion arms, upon which it is carried in bearings on standards or other supports. Upon one of the trunnions is keyed a toothed wheel, which gears with a rack (Fig. 103) attached to a hydraulic ram, by the movement of which the converter can be rotated on its bearings through 180° to 300°. The other trunnion is hollow, and connects by the pipe P (Fig. 103) with the blast-box B at the bottom of the converter. This is a compartment into which the blast is led through the hollow trunnion, and passes through the metal by means of clay tuyères T passing through the upper or guard-plate of the blast-box and the lining of the vessel. The vessel is lined with about 9 to 12 inches of ganister on the sides, and 18 to 20 inches on the bottom, introduced as described, p. 58. The tuyères are slightly conical in form, and are about 22 inches long. They are made of fireclay, and contain from 10 to 12 $\frac{3}{8}$-inch holes, running in the direction of the length, by which the air passes from the blast-box to the vessel. They pass up through holes in the guard-plate, against which they are pressed by suitable stops, and are embedded in the ganister lining the bottom. They only stand out slightly from the surface.

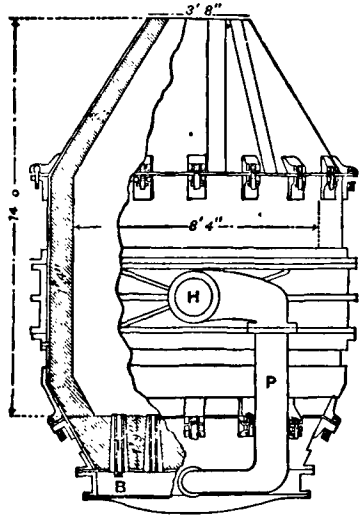


FIG. 103.—Bessemer converter, as used in basic process.

If a tuyère proves faulty in work it can be removed and replaced by taking off the bottom plate, knocking it out, and pushing up a new one in its place, a little slurry of ganister being run round from the inside to make the joint secure. After drying and heating the converter is again ready.

Converters with detachable interchangeable bottoms are now commonly employed, so that little delay is occasioned by the removal of a worn-out or faulty one, and the substitution of a newly prepared bottom. The vessel itself is also made in sections, as shown, and duplicate parts are kept ready for use.

Method of conducting the Process.—The pig iron to be treated is melted in cupolas, or is taken direct from the blast furnace, or from a metal mixer[1] to ensure uniformity. The converter, previously heated, is turned on its side, and the metal run in. The full charge lies below the level of the tuyères when in this position. The blast, at a pressure of from 20 to 25 lbs., is then turned on, and afterwards the vessel is rotated into a vertical position. The metal now flows over the bottom, and the air passes up through it, the high pressure preventing it running into the blast-box. At first only a short, yellowish-red flame is seen at the mouth of the converter, accompanied by sparks. During this period the temperature rapidly rises. The silicon is being rapidly oxidised to silica (SiO_2) and manganese to oxide; the silica, combining with oxides of iron and manganese, forms silicates. The flame gradually becomes larger and more luminous, and is accompanied by showers of brilliant sparks, consisting of slag and particles of iron. This corresponds to the "boiling stage" of the puddling process, and is known as the *boil*. The violence of the disturbance of the metal is due to the rapid oxidation of the carbon with the production of carbon monoxide, which escapes. During this part of the process, the pressure of the blast is reduced. The luminosity and volume of the flame gradually diminish, and in the third or "fining" stage, during which the remainder of the carbon and manganese are being removed, it fades to a pale amethyst tint, and is nearly transparent. There are also fewer showers of sparks. In from fifteen to twenty minutes from the commencement of the blow, the flame suddenly shortens or "drops." This marks the almost complete removal of the carbon, and if blast be further continued, great loss from oxidation takes place, and the quality of the metal is rendered much inferior. The vessel is accordingly turned down and the blast shut off. A weighed quantity of spiegeleisen, previously melted in a cupola, is added to the metal as it lies in the converter, from a ladle. This addition is attended by a violent outburst of flame and considerable agitation of the metal. The spiegel imparts to the iron the requisite amount of carbon to produce steel of the desired temper, and also sufficient manganese to restore the malleability, which, as before noted, is always lost when malleable iron in a molten state is subject to oxidising influences. For steel of very low temper, ferro-manganese is employed, in order to introduce the necessary amount of manganese without adding too much carbon. This is added solid. After standing a few moments to allow the slag and metal to separate, the converter is turned down and the steel run from its mouth into the ladle. Enough slag to cover the metal and keep it hot is also allowed to flow into the ladle. The converter is then turned completely over, and the slag allowed to run

[1] *The mixer* is a large receptacle, heated or otherwise, in which the metal from various blast furnaces is stored in a molten state. The converters or steel furnaces are supplied from it. Greater uniformity in composition is thus secured. Metal mixers for open-hearth work are large rolling furnaces.

out. All the movements of the vessel, as also the blast, are regulated by a workman situated on an elevated platform at some distance from the converter, the progress of the operation being judged from the appearance of the flame.

The ladle to which the metal is transferred is mounted as shown (Fig. 104) on a hydraulic crane, in the centre of the casting pit, which is circular. The converters are situated at the side of the pit.[1] The ladle can be raised and lowered, can be made to travel round the pit, to and from the centre, and also turned over to empty slag. It is lined with ganister, and heated by a fire made in it before receiving the metal. The teeming is effected from the bottom, through a hole

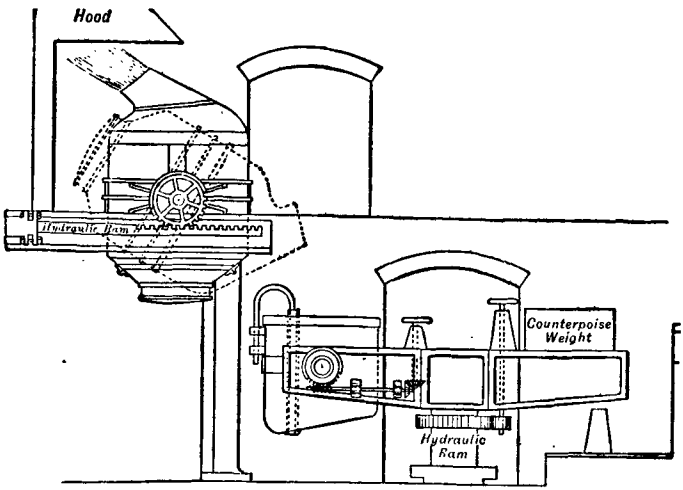


FIG. 104.

closed by a fireclay stopper, which is raised and lowered by an iron rod protected with fireclay tubes and connected with a suitable lever or other means of operating and control.

The moulds are of cast iron, open top and bottom, and more or less tapering. They are arranged round the side of the casting pit, standing on an iron plate. The usual practice is to fill each mould separately from the top, but sometimes the moulds are arranged in groups, round a central one somewhat taller than the rest. The bottom of this is connected, by a system of fireclay tubes opening upwards, with the bottoms of the others. The metal is run into the central or feeding ingot and is conveyed to the others by the clay passages. It gradually rises in the moulds until they are all filled. Sounder ingots are said to be obtained in this way. In all cases they are stoppered down with sand and a plate, as previously described.

Chemical Changes in the Bessemer Process.—The oxidation of the impurities in the pig is effected by oxide of iron, formed by the air blown in, so that

[1] The arrangement of plant varies considerably. In many cases the casting pit is omitted, the moulds standing practically on the ground level.

the chemical reactions are similar to those taking place in puddling. Being in a fluid state, and thoroughly agitated by the passage of the air, silicon and manganese, being most oxidisable, are much more largely attacked than other impurities in the first stage of the process, and are reduced to about 0·5 per cent. In the subsequent stages they are reduced to about 0·01 or 0·03 per cent. During the boil the carbon is reduced to below 1 per cent., and in the fining stage to below 0·1 per cent. Manganese is attacked from the beginning and throughout the process, the oxide formed combining with the silica and forming silicate, which passes into the slag. The phosphorus, as shown by its absence from the slags, is unattacked, and the steel consequently contains a higher proportion than the original pig iron, since a loss of some 10 per cent. occurs on the weight of pig employed. This is due, as already noted on p. 60, to the siliceous nature of the lining. The iron employed must therefore be free from phosphorus. Sulphur also is not removed.

The blast is used cold, and yet the temperature gradually rises as the process proceeds. This increase of heat is due to the oxidation going on, principally of the silicon and the iron. The amount of silicon present is less than the carbon, but in burning, a solid substance (SiO_2), which remains behind in the converter, is produced, and all the heat generated is communicated to the contents of the vessel (save such as is carried away by the nitrogen of the air blown in). The combustion of the carbon generates gaseous bodies which, escaping, carry away much of the heat. Manganese, like silicon, yields a solid product of combustion, and accounts, when present, for some of the heat.

During the blow the iron is oxidised and becomes "burnt," and is rendered brittle and unworkable. The manganese in the spiegel added combines with the oxygen, forming manganous oxide (MnO), and passes into the slag. A slight excess is always employed to ensure the complete removal of the oxygen. This, with the carbon contained in the spiegel, enters the steel. Bessemer and open-hearth steels always contain manganese. The amount should not exceed 0·7 per cent.[1]

The metal employed is grey pig iron, and should contain about 2 to 2½ per cent. of silicon, and be free from sulphur and phosphorus. Iron smelted from pure ores, such as red hematite and magnetite, and known as *Bessemer pig*, is employed. With the rapid, continuous working practised in America—a fresh quantity of pig being run in immediately after teeming the previous charge, so that no loss of heat occurs—pig containing not more than 1 per cent. of silicon is satisfactorily treated. Excess of silicon increases the amount of loss, and some may remain in the steel.

The process described above is commonly known as the *acid* process, from the siliceous nature of the ganister lining. The slag consists of silicate of iron and manganese. As already shown, iron containing phosphorus cannot be treated under these circumstances. By substituting a lining of basic material, phosphorus as well as other impurities may be removed.

The Basic Bessemer Process is conducted in a vessel similar to that already described, but generally with a straight neck, so that the metal can be poured from either side, and the converter can be completely rotated by worm and wheel gearing, actuated by hydraulic engines attached to the standards or by other means.

The converters are made in sections, which can be readily secured together by pins and cotters (see Fig. 103), so that if the lining of any portion gives way another similar part can be substituted without delay, an overhead travelling crane which commands the converters, and hydraulic tables under each converter, being provided for raising and lowering the parts.

[1] One per cent. is allowed in rails and tyres and in "free cutting steel" sometimes reaches 1·25 per cent.

The lining employed consists of calcined dolomite or magnesite (see p. 60), and is about 14 to 16 inches thick on the sides, and 24 inches on the bottom. Loose tuyères are sometimes employed, but generally they are formed by ramming the lining material round steel spikes, which are withdrawn when the bottom is rammed up, and thus form free passages for the air. The process differs somewhat from the ordinary "acid" process. Before running in the iron, a quantity of lime, equal to about 15 per cent. of the charge, is introduced, with a little coke, into the converter and blown hot.[1] The charge is then run in, in the usual manner, and the blow proceeds as before up to the point at which the flame drops. Instead of stopping the process here, the blast is continued for some two or three minutes longer to eliminate the phosphorus. The vessel is then turned down, and a sample taken with a spoon, hammered out, cooled, and broken. From the fracture and malleability, the workman judges how long the blow must be continued to complete the elimination of phosphorus. A crystalline fracture indicates that the phosphorus is not completely removed, and the vessel is turned up, and the blowing continued until the metal is dephosphorised. A second sampling may be necessary.[2]

The slag is then run off, to prevent precipitation of phosphorus into the metal by reduction from the slag when the carbon is added. Spiegel and ferro are then added in the usual manner, and the charge transferred to the ladle, and thence to the moulds. In some cases, where hard metal is required, the carburisation is effected by grey pig iron free from phosphorus, added in a molten state to the metal in the ladle, ferro-manganese being afterwards added.

The oxidation of impurities during the blow, up to the dropping of the flame, proceeds as in the acid process, but, owing to the nature of the lining and the basic character of the slag, some phosphorus is also removed. In the after-blow the residue of the phosphorus is oxidised, and, combining with lime, forms calcium phosphate, and passes into the slag. This frequently contains as much as 30 per cent. of phosphates of lime and magnesia, together with 8 to 10 per cent. silica, 10 per cent. oxide of iron, sulphur, and some oxide of manganese. It amounts to about 20 per cent. of the charge, and on account of the phosphates present is ground up and used as manure, under the name of "basic slag."

If the pig iron treated contains much silicon, the charge becomes too hot, and the corrosion of the lining is increased. Since, under ordinary conditions, the presence of silicon is essential to provide heat by its oxidation, some substitute is necessary in basic Bessemer pig. This is found in the phosphorus, and as much as 2·5 to 3 per cent. of that element is often present. It lowers the melting-point of the metal

[1] Lime in small pieces is often fed into the converter during the process. It is allowed to fall into the mouth during the blow. By this means the wear on the lining is reduced.

[2] The time during which the blowing is continued after decarburisation is known as the "*after-blow*." During its continuance, red-brown smoke issues from the converter.

until decarburisation is complete, and thus less heat is requisite in the earlier stages. By its oxidation in the after-blow, it produces the high temperature necessary to maintain the iron in the fluid state. As with silicon, the product of burning is a solid, and remains in the vessel. Some of the slag is returned to the blast furnace to increase the phosphorus in the pig. About 1 per cent. of silicon is necessary in the iron, or the blow will be too cold and slow. The presence of from 1 to 2 per cent. of manganese is also advantageous.

The removal of the phosphorus depends on the basicity of the slag, and hence the addition of lime in the converter. This also diminishes the wear on the lining. The loss amounts to about 15 per cent.

The charge of a converter ranges from 5 to 15 tons, and the operation lasts from 15 to 25 minutes, according to weight and circumstances.

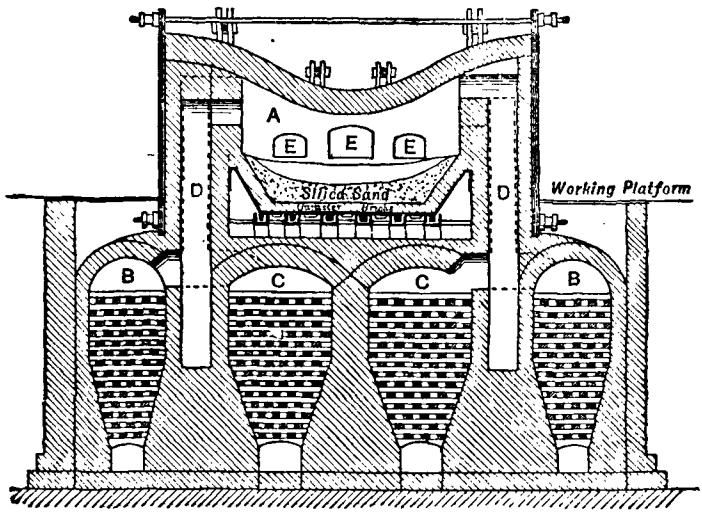


FIG. 105.—Siemens regenerative furnace. Longitudinal section.

Transfer processes are often employed when the pig iron contains much silicon. Part of the metal from the blast furnace is treated in an *acid lined* converter to remove the silicon and then removed to a large metal mixer into which the remainder of the iron from the furnace has been put, without treatment. The resulting product contains enough silicon to start the blow satisfactorily, and excessive wear on the linings is prevented.

The **Tropenas** converter is a small vessel holding about a 2-ton charge. The vessel is ganister lined. The tuyères are situated at the side of the converter, and by changing the inclination of the converter the blast is made to blow on the surface of the metal. It is used for making steel castings.

Open-hearth Processes.—Under this heading are included processes conducted in *regenerative gas furnaces* of the Siemens type (see Fig. 105), the bed of which may be composed of silica sand (acid), or of magnesite, dolomite, or chromite (basic).

Siemens Regenerative Furnace is shown in Figs. 105 and 106. The furnace is a double-ended, reverberatory, gas-fired furnace. The furnace chamber, A, communicates at either end with the chambers B B, C C, by means of the ports and flues D D. The chambers

are filled with chequer brickwork. The chequers are alternately heated by the passage of the hot gases from the furnace descending through them on their way to the chimney-stack, and the heat retained is subsequently given up to the cold air and gas passing upwards through them on their way to the furnace. The chambers are worked in pairs, the gas and air being heated in separate chambers. One pair of chambers is being heated up while air and gas are passing through the other pair. The smaller chambers, B, are the gas chequers, and C the air chequers; E E E are the working doors; F is the chimney-flue; G the gas-supply culvert; R R the valves for reversing the direction of the gas and air; L the launder or spout for conveying the metal into the ladle; P is the casting pit. The

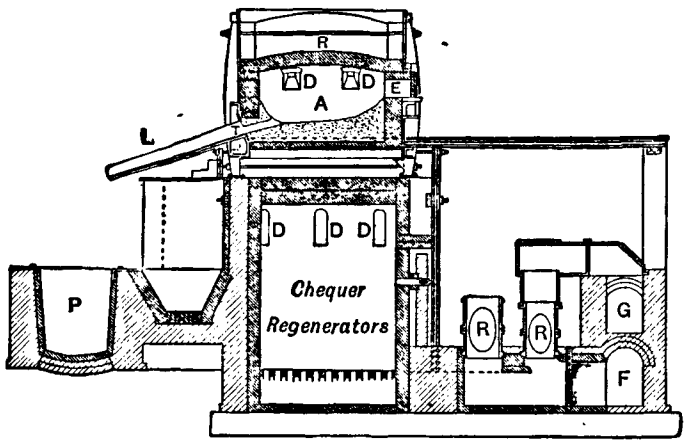


FIG. 106.—Cross-section of furnace.

direction of the air and that of the gas are reversed every half-hour. In this way the chequers are kept at a high temperature, and the gas and air coming to the furnace develop a much higher temperature than if supplied cold.

The Siemens Process.—This process is analogous to the "pig boiling" puddling process, the decarburisation of the metal being effected by *pure* oxidised iron ores added to the fused metal in the bath of the furnace On this account it is sometimes described as the "pig and ore" process.

The pig iron, to the extent of 5 to 40 tons, is introduced on the bed of the furnace and melted. In modern practice molten metal is commonly employed. This is brought from the metal mixer in a large tipping ladle and emptied into the furnace. After fusion, additions of red hematite, roasted pottery mine, or other pure oxidised ores are made from time to time, which effect the oxidation and removal of the silicon, carbon, and manganese in the pig in the same manner as in puddling.

At the high temperature attainable in these furnaces, 1700° C., however, the metal remains molten even after decarburisation is complete, and its conversion into steel is effected by the addition of spiegel and ferro, as in the Bessemer and Basic Bessemer processes. The time occupied is, however, much longer, extending sometimes to 10 or 14 hours with large charges. This permits of more perfect control over the composition of the steel produced, as samples can be taken from time to time, and the character and carbon contents of the metal rapidly determined. When the carbon has been reduced below 0·1 per cent., spiegel is added, the tap-hole is broken open and the metal run into the ladle. Ferro-manganese, broken into small pieces, is added in the ladle as the metal flows out, to replace that lost by oxidation in the furnace, and to make up the amount necessary to restore the malleability and carburise the iron. (For carburisation with anthracite, see p. 198.)

In the decarburising stage, the metal boils violently, and is thus brought into contact with the oxidising slags and the atmosphere of the furnace, but becomes quiet towards the end of the operation. The addition of spiegel causes it to again become lively, and the metal is tapped on the boil.

In some cases only the excess of carbon present in the bath after melting is removed. When the carbon tests show that the carbon has been reduced below the desired limit sufficient pure pig iron—*i.e.* nearly free from sulphur and phosphorus—previously heated to redness, is added to raise the carbon to the required specification. Ferro-manganese is added as the steel runs from the furnace into the ladle. This method of working, "catching the metal on the drop" and "pigging back," saves time and fuel. The operation is so carried out that any excess of silicon is removed before the carbon.

The yield is some 2 or 3 per cent. in excess of the pig iron charged, owing to the reduction of the ore added to decarburise it. A cutting oxidising flame is employed in the earlier stages.

Siemens-Martin Process.—In this process the percentage of carbon to be removed from the metal is diminished, by melting the pig iron with scrap wrought iron or steel introduced into the furnace at the same time, or previously heated and charged into the bath of molten pig iron. Scrap to the extent of 8 or 10 times the weight of pig is frequently employed. The charge, after fusion, contains less than 1 per cent. of carbon. The amount of scrap added depends on the greyness of the pig. No ore is added, and the decarburisation is effected by the oxide formed on the scrap during melting, and the atmosphere of the furnace, which is oxidising. The bath is sampled from time to time, and, when the carbon has been sufficiently reduced, spiegel and ferro-manganese are added as before. The loss amounts to about 7 or 8 per cent. of the metal charged.

A combination of the two processes is commonly used in this country, pig iron, scrap, and ore forming the furnace charge. It affords a convenient method of utilising scrap.

Basic Open-hearth Processes.—In furnaces with sand bottoms the pig iron employed must be of Bessemer quality, but with basic bottoms phosphoric pig can be treated. As in the basic Bessemer process, lime is charged in the furnace, and samples are taken from time to time and tested.

As the phosphorus is not required as a heat-producer, the less there is present the better.[1] Pig containing about 1·5 to 2 per cent. is satisfactorily treated, but the presence of manganese up to 2 or 3 per cent. is also desirable. In dephosphorising, it is sometimes necessary to make small additions of ferro-manganese and pig to introduce a little carbon. The carbon monoxide formed produces the necessary agitation to bring the metal into contact with the basic slag. The metal obtained by any of these processes is dealt with as in the Bessemer process.

Direct Recarburisation.—In addition to the use of pig iron, spiegel and ferro, for introducing carbon into the metal, recarburisation is now often effected by the use of anthracite and coke. This is put at the bottom of the ladle or thrown into the stream of metal as it runs from the furnace. Paper bags carrying 7 to 10 lbs. of powdered anthracite or coke are a convenient means to employ for the addition. About 60 to 70 per cent. of the carbon may be taken up if judiciously added (Darby's Process).

Degasification.—When the process is completed the molten steel usually contains considerable amounts of gases in solution. These consist of carbon monoxide, hydrogen, and nitrogen. (It is claimed that even free oxygen may be present.) If the gases are not removed or caused to remain in solution in the metal while and when it solidifies, the metal will be "wild" and boil or froth up on pouring. The ingots when solid will be unsound. This may not be confined to the top, which is generally more or less honeycombed and has to be removed. Such ingots produce faulty, unreliable, and seamy steel. Sound ingots can only be obtained by the addition of substances which either cause the gases to escape while the steel is molten or to remain in solution and prevent the formation of cavities—blow holes. Manganese, silicon, and aluminium are added for this purpose. The two former are used for "killing" both in the furnace and ladle. Aluminium is used in the ladle.

"Rimming Steel" is a description given to low carbon mild steels which are not completely "killed." Considerable amounts of gas with agitation are given off during solidification. This agitation promotes the floating out of non-metallic impurities, but also permits greater segregation towards the liquid centre of the ingot.

Casting.—The casting pits are generally rectangular, and the ladle, mounted on a carriage, travels on rails over the tops of ingot moulds.

Attempts have been made to combine the rapidity of the Bessemer processes with the certainty of the results obtained in the open hearth processes.

A combination of the two processes is followed by blowing the metal in a converter till the carbon is sufficiently reduced, and then teeming it into a heated Siemens furnace, and completing the decarburisation in the ordinary manner.

[1] If a sufficient amount is not present the slag will not be useful as a fertiliser.

Hollow rabbles introduced into the molten metal on the hearth, by which air or steam can be blown through it, are in use to a limited extent. Clay-covered iron tubes are employed. At Ruhort, 3 such tubes, each containing 3 holes, are employed. The blast is continued for from 10 to 20 minutes, and the temperature rises higher than in the ordinary open-hearth process.

The Bertrand-Thiel and Talbot processes are modifications of the open hearth process.

In the former the pig iron is first treated in a basic-lined "primary" furnace for the removal principally of the silicon and phosphorus, and is then run into a "secondary" furnace at a lower level for decarburising and finishing. The secondary is hotter than the primary.

In the Talbot process a single furnace capable of holding up to 300 tons of molten metal is employed. It is of the Wellman tilting type, and pours the metal from a spout instead of running from an ordinary tap-hole. This spout, when the furnace is not turned down for emptying purposes, rises above the level of the metal contained in the bath. Supposing a charge to be ready for teeming, instead of running the whole of the metal out, approximately only one-third is removed.[1] The furnace is then rolled back, oxide of iron added to the slag, and molten pig iron equal in weight to the steel just removed, run in. In a few moments a violent reaction ensues between the oxide and the impurities in the pig, resulting from the large amount of heat stored in the remaining charge and its high temperature. The bulk of the foreign elements is removed, and the steel only requires to be finished. The output is greatly increased.

The steel produced by the Bessemer, Siemens, and analogous processes is generally of a mild character, containing less than 0·6 per cent. of carbon, and is employed for rails, 0·3 to 0·6 per cent. of carbon; boiler-, bridge-, and ship-plates, 0·2 to 0·25 per cent. of carbon; armour-plates, guns, and other purposes where metal of high ductility, elasticity, uniformity, and strength are required, and also for castings.

The honeycombing previously noted in connection with crucible steel is more marked. Stoppering down is resorted to, and in some cases pressure is applied.

In Whitworth's fluid compressed steel, the ingot, after running in a mould of special construction, was placed on the table of a hydraulic press and subjected to a pressure of from 6 to 20 tons to the square inch. A contraction of 1½ inch per foot takes place, and a sounder ingot results.

In the production of sound steel castings, various physics are resorted to. The introduction of from 0·2 to 0·3 per cent. of silicon in mild tempers, and from 0·3 to 0·4 per cent. in harder tempers, tends to increase the solidity of the casting. It is introduced as ferro-silicon or ferro-silicon manganese—alloys of silicon with iron and manganese, but containing also carbon. Aluminium is also employed for the same purpose.

Treatment of Ingots.—The ingot moulds, after the solidification of the metal, are lifted by cranes situated at the side of the casting-pit, and the ingots allowed to cool; or removed immediately to "soaking-pits" or soaking furnaces in which they are kept hot till required for rolling.

These soaking-pits consist of a series of vertical chambers of fire-brick below the ground-level, arranged in a double line, each capable of holding an ingot, and covered with a tile and commanded by cranes. The ingots are removed to them immediately they have solidified.

[1] In practice the amount varies; it may be greater than one-third.

The interior of the ingot when stripped is much too hot to permit of its being rolled at once, and the excess of heat gradually soaks out and distributes itself uniformly through the mass. They can be kept hot for some time, and removed for rolling as required. Little heat is lost, and reheating of the ingots is avoided. Oxidation is prevented by the gases exuding from the metal, which are of a reducing character (p. 188).

The difficulty of keeping up a supply of ingots to keep the pits hot has led to the use of "soaking-furnaces." These are gas-fired furnaces with the roof at floor level. The roof of the furnace is in sections, mounted on rollers on a rail track. Thus a gap can be opened at any point over the whole length for the introduction or removal of ingots by a travelling crane.

The rolling of mild steel is effected in a manner similar to that followed for malleable iron.

Use of Spiegel and Ferro-manganese.—In carburising Bessemer or open-hearth steel, the richness in manganese of the alloy used is mainly determined by the amount of carbon desired in the resulting steel. If a steel very low in carbon is required, an alloy (ferro-manganese) containing much manganese is employed, to introduce the needful amount of that element, without at the same time adding an excess of carbon.[1] For higher carbon steel, spiegel and ferro containing less manganese are employed. Steels containing a higher percentage of carbon than 0·5 may be made, as in the Darby process, by carburising with gas carbon, anthracite, etc. The molten metal is run into a ladle containing the recarburising material, which it dissolves. An undue proportion of manganese is thus avoided.

In addition to pig iron speigel, ferro-manganese, silico-spiegel, silico-manganese, ferro-silicon, powdered anthracite or coke, and aluminium already mentioned for the purpose of deoxidising or carburising the metal, carborundum (silicon carbide, SiC_4) is used for imparting carbon and silicon in the production of high carbon steels. Calcium silicide has also been used as a deoxidant and desulphuriser. Silicon and aluminium both reduce unsoundness, diminishing the number of blow holes by promoting the solution of the gases.

Constructional Alloy Steels in the open hearth furnace. Alloying metals may be added successfully in the open hearth process if due attention be paid to their oxidisability, fusibility, and special properties.

Nickel may be added early in the process with the charge or after melting. It is not specially oxidisable and its melting-point (1452°C.) is within the temperature during the melting period and its density is similar to that of iron.

On the other hand, chromium is highly oxidisable and the loss would be great if added early in the process. The addition is made in the furnace just before recarburising after ferro-silicon has been added to deoxidise the metal. Metallic chromium is used, as carbon-free as may be necessary. Ferro-chrome varies from 65 per cent. Cr. and 9 per cent. C. to pure chromium.[2] Addition of chromium in the ladle is less satisfactory.

[1] The amount of *carbon* present in spiegel and ferro shows no *great* variation.

[2] For low percentages a mixture of ferro-silicon and chrome iron ore is now being used. The silicon reduces the chrome oxide in the ore and the reduced metal enters the steel.

Molybdenum—the use of which is now increasing—may also be introduced in two ways, dependent on circumstances. Ferro-molybdenum contains from 50 per cent. molybdenum upwards with a little silicon. As the melting-point of the alloy is high—1500° C.—the addition is made in the furnace as early as convenient. Some loss occurs.

Molybdenum being mainly obtained from molybdenite—the sulphide—the metal must be watched for sulphur content. It may contain up to 0·2 per cent.

Calcium molybdate added in the furnace is also employed for direct introduction, as in the case of chromium.

Ferro-vanadium is usually added in the ladle. It is important to prevent contact of the metal with the slag. The ferro may contain up to 50 per cent. vanadium, 5 per cent. silicon, and 3 per cent. carbon.

Electric Furnace Practice.—Electric arc-furnaces used in steel-making enable higher temperatures to be attained without undue exposure to oxidising atmospheres.

They are usually of a tilting type and consist of a casing of steel plate lined with acid or basic refractory material. The electrodes are introduced through openings in the roof and provided with mechanical and automatic controlling devices for striking and regulating the arc, the length of which enables temperature to be controlled and maintained uniform. Openings are provided for charging and repair purposes and a spout for removal of slag and metal by tilting as required. Current is supplied at low voltage, and if the voltage at the source of power be high, it passes through a step-down transformer.

The high temperatures possible enable very highly basic or acid slag to be employed at will, and the facility with which heat is produced and controlled allows slags to be changed as required.

The **Heroult Furnace** is shown in Figs. 107, 108. The furnace chamber D has a magnesite bottom A and can be tilted on E through the rod F. B is the pouring spout opposite the charging door. Two electrodes C, 17 inches in diameter, pass through water-cooled openings in the roof and are supplied with current through the leads seen in Fig. 108. In the Heroult furnace there is no electrode in the furnace bottom.

The arcs are in series. The electrodes are brought down and short arcs are struck between the charge and the electrodes.

Furnaces working on single-phase circuits with two electrodes, and furnaces with three electrodes operating on three-phase circuits, are in use.

The Greaves Etchells Furnace—also a tipping furnace—has an electrode in the hearth also and the current passes through the material in the bath. The electrode is a copper plate embedded in the hearth. The lining is calcined magnesite, or dolomite, which becomes conducting when hot, but is non-conducting when cold. This plate is first covered with a layer of tar-bound graphite followed by a 4-inch layer of coke dust and tar, on which the ordinary basic lining is rammed and heated till it becomes conducting. The electrodes, of which as

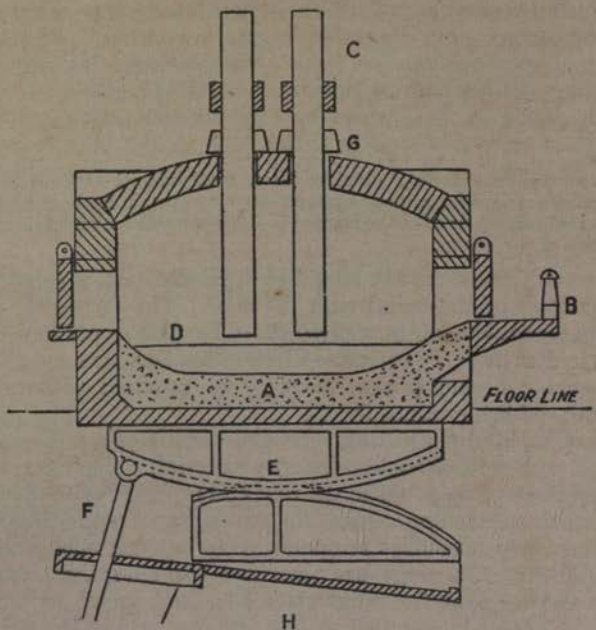
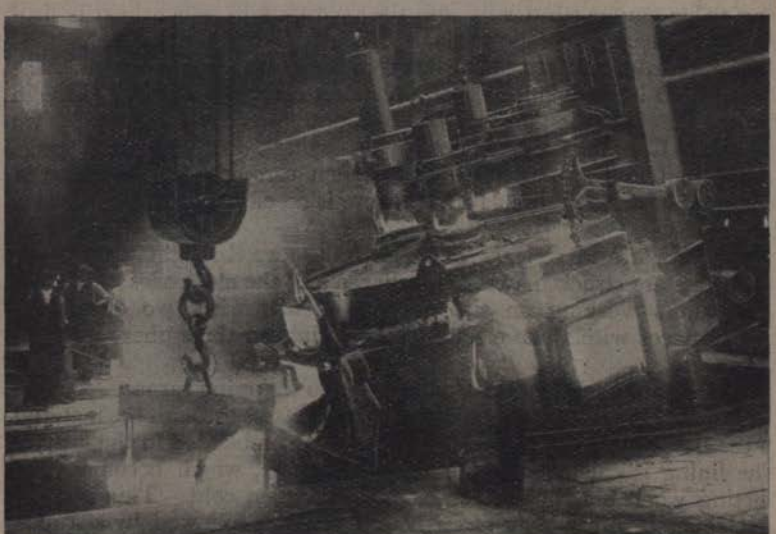


FIG. 107.—Sectional View of Heroult Furnace.

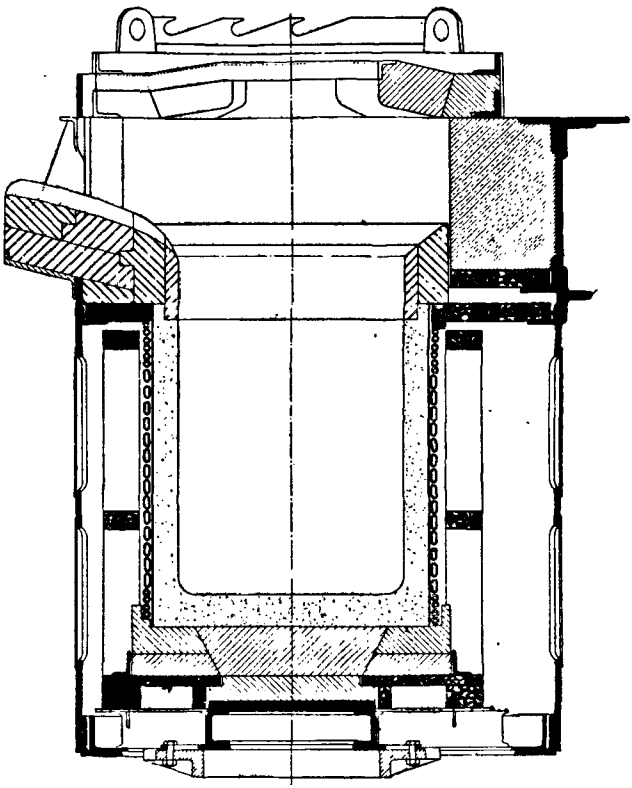


Courtesy of Electric Furnace Co., Ltd.]

FIG. 108.—Heroult Furnace (pouring).

many as eight are used, are coupled in pairs, each pair having a separate electric supply. The hearth electrode is a common return for all circuits.

In making steel in arc furnaces complete elimination of sulphur and phosphorus may be secured. The high temperature enables



Courtesy of Electric Furnace Co., Ltd.]

FIG. 109.—High Frequency Melting Furnace (section).

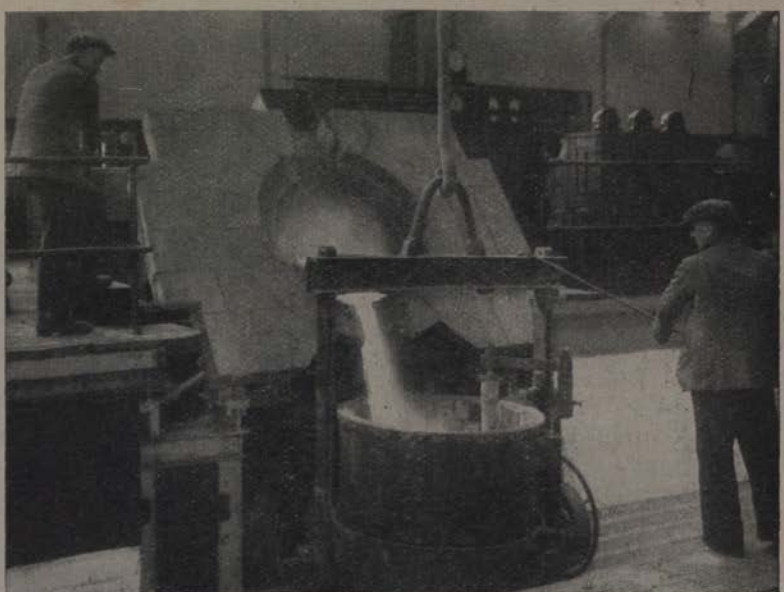
the slag to be made basic without being oxidising. With an oxidising slag (containing oxide of iron) at high temperature, lime will not decompose iron or manganese sulphide.

If the oxidising slag be substituted by a non-oxidising basic slag of suitable composition, and reducing conditions established, sulphide of calcium will form. This change of conditions is effected by running off the first slag when oxidation is complete, and making up a fresh basic slag by the introduction of lime and fluorspar free from sulphur. When fully fluid ferro-silicon is added. At the high temperature,

if the slag be sufficiently basic and fluid, the sulphides of iron and manganese are decomposed and calcium sulphide formed, which passes into the slag.

Coke and calcium carbide are sometimes added with the flux, followed by ferro-silicon. This treatment also deoxidises the metal.

Alloy additions, if required, are then made, the metal allowed to rest quietly for a short period with the current cut off and tapped. While resting in the furnace any included particles rise to the surface



Courtesy of "Metallurgia."]

FIG. 110.—Pouring steel from a high frequency furnace.

and pass into the slag. Metal when tapped from an electric furnace is often too hot to pour, and is allowed to stand till a proper temperature is reached.

Arc furnaces with capacities up to 60 tons have been operated.

High Frequency Electric Furnace.—Many of the small arc furnaces in use for the production of alloy steels have been displaced by the introduction of high frequency coreless induction furnaces. In these powerful currents, alternating very rapidly, produce induced eddy currents in the metallic material of the charge, the resistance of which causes heat to be produced. The resistance increases with the temperature, and in the later stages heat is developed more rapidly. Furnaces from 7 cwts. to 7 tons are in use. Fig. 109 shows a section of the furnace part. The steel casing in which the furnace is built is

mounted so that it can be tilted to pour the metal from the spout in such manner that at any angle the metal stream is in the same vertical plane.

The heating unit consists of a spiral coil of flattened copper tubing conveying the current. Water is kept flowing through the coil to prevent overheating of the conductor.

Inside this coil for small operations a crucible suitably shaped with a pouring spout is placed and receives the charge. With larger furnaces, such as that shown, Fig. 109, the lining is formed in position

Courtesy of "Metallurgia."]

FIG. 111.—Teeming steel from high frequency furnace.

by placing inside the coil at a suitable distance a metal former of the internal size and shape of the lining. Dry refractory lining material is placed under and round this metal former.

When the current is switched on the metal former becomes heated and ultimately melts. The lining is consolidated by the heat and a large crucible is made *in situ*. The coil is surrounded by lagging material.

Elaborate electrical arrangements are required. A high frequency converter including a transformer to step the voltage up to that required for the condensers, a spark gap, a bank of condensers and safety gaps and switch gear being included, with, of course, the necessary electrical measuring instruments and fuses. Furnaces of this type have largely replaced melting holes for crucible steel

Fig. 110 shows such a furnace being poured at the works of S. Fox & Co., Sheffield.

The advantages are obvious. Melting steel out of contact with furnace gases, coke, and carbon electrodes, and with perfect temperature control robs steel melting of many of its troubles and makes many difficult operations simple. The furnaces are in use for melting purposes for ingots and castings, especially low carbon metals and alloys, *e.g.* magnetic alloys and specially low carbon stainless iron, among other purposes.

CHAPTER XII

COPPER

Physical and Chemical Properties.—This metal possesses a fine red colour, and is characterised, when pure, by extreme toughness. Its hardness is slightly under 3. It is more malleable but less ductile than iron. In the cast state its tenacity is only about 9 to 12 tons, but after rolling this is increased to from 15 to 18 tons, and by wire-drawing to 30 tons. Its modulus of elasticity as wire is 17,000,000, that of iron wire being 25,300,000. At temperatures higher than 337° C. the tenacity and elasticity of copper and most of its alloys are greatly reduced. Alloys with nickel are least affected. Its specific gravity is 8·6, but by rolling, etc., is increased to 8·8. Its melting-point is about 1084° C. Pure copper[1] is an excellent conductor of heat and electricity, but the presence of minute quantities of impurity greatly impairs this quality. The metal is unaltered in dry or moist air free from CO_2 and acid vapours. A green coating of basic salts forms when these are present.

On heating in air, a series of coloured oxide films are formed, and at a red heat a black scale of oxide, which detaches itself from the metal if suddenly cooled. The outside of this scale consists of black cupric oxide (CuO), but the inner layers principally consist of red cuprous oxide (Cu_2O). Cupric oxide is reduced to cuprous oxide when fused with copper. Copper dissolves cuprous oxide when molten, and is rendered dry and brittle. "Dry" copper breaks with a dull, brick-red fracture. In practice the metal is toughened by covering with anthracite, and stirring it with hard-wood poles. Hence the term "poling." The reducing gases from the wood agitate the metal, and, in conjunction with the anthracite, reduce the oxide, and the metal assumes its normal tough condition.

If the copper is not chemically pure, it is possible to continue the poling too long, and the metal again becomes dry and unmalleable. By leaving a little of the oxide unreduced, the harmful effects of the impurities are neutralised to some extent. It is described as "underpoled," "tough cake," and "overpoled," according to its condition. Pure electrotype copper cannot be overpoled. *Underpoled* copper contracts greatly on solidifying, and a furrow is formed down the middle of the ingot. The cuprous oxide in the copper forms a eutectic containing 3·8 per cent. of cuprous oxide. Hence the settling down on cooling. *Tough cake* copper casts with a nearly flat surface,

[1] The addition of silver to 0·1 per cent. prevents softening of work-hardened copper on annealing. This is being applied in the production of armature bars and switchgear fittings. Conductivity at low temperatures is high.

while, if *overpoled*, the metal rises in the mould, and a ridge is formed, due to the escape of gas liberated at the moment of solidification.

If "tough" copper be exposed to reducing conditions for a prolonged period it becomes brittle. The condition is known as "gassed" copper. (Fig. 112.)

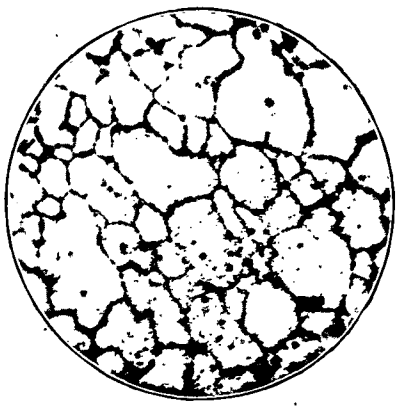


FIG. 112.—Gassed copper.

Very small quantities of sulphur, antimony, and bismuth seriously impair the malleability, ductility, and tenacity of copper. Tin, nickel, cobalt, and iron are also often present in commercial copper. They render the metal lighter in colour and somewhat harder, but do not lower its tenacity.

Copper has greater affinity for sulphur and less affinity for oxygen, than iron has. Two sulphides are known. *Cuprous sulphide*, Cu_2S, is produced by heating copper and sulphur together, and is the "white metal" of the copper smelter. It also occurs naturally in various copper ores.

Cupric sulphide (CuS) is precipitated when a soluble sulphide is added to a solution containing copper.

The sulphides are *not* completely reduced by iron or carbon. When heated in air, sulphur burns off as sulphur dioxide, SO_2, and a mixture of oxides and sulphate, in proportions varying with the conditions, results.

Sulphate of copper is soluble in water, and is decomposed when strongly heated. It requires a higher temperature to decompose it than sulphate of iron. When sulphide of copper is heated with oxide or sulphate, the sulphur and oxygen pass off as SO_2 and the metal is reduced.

$$Cu_2S + 2Cu_2O = SO_2 + 6Cu$$
$$Cu_2S + CuSO_4 = 2SO_2 + 3Cu$$

Copper and phosphorus combine readily, forming phosphide of copper.

Bronze includes all alloys of copper and tin.

The effect of tin in whitening copper is greater than that of any other metal. The alloys have a lower melting-point, and cast more soundly than copper. The toughness, tenacity, and other properties vary with the composition of the alloy. (See p. 349.) Tin alloys show a great tendency to liquate. The term is also applied to many other copper alloys, *e.g.* nickel-bronze, etc.

Brass includes all alloys of copper and zinc. The effect of zinc in whitening copper is much less than tin, and hence wider range of colour and composition is possible.

The malleability and tenacity of certain of these alloys is little inferior to copper, *e.g.* Dutch metal is beaten into thin leaves in imitation of gold, and brass, for wire and plate, has a tenacity of 8 or 9 tons cast, which, after rolling and wire-drawing, varies from 20 to 26 tons. (See Alloys, p. 348.)

Ores of Copper.

Native copper often occurs with copper ores, sometimes in masses, as in the Lake Superior district, but more often in arborescent and reticulated forms. In the Calumet, Hecla, and other mines, about 2 per cent. of native copper, mainly in small grains, is distributed through the rock.

This is extracted by dressing processes, and smelted and refined at one operation. The copper Barilla of Chili was a deposit of grains of copper, oxidised on the surface. Native copper is usually very pure.

Cuprite, *red oxide of copper, cuprous oxide* (Cu_2O), occurs, crystallised and massive, in Thuringia, Chessy, near Lyons, Cornwall, Siberia, United States, Cuba, Australia, etc. It contains 88·8 per cent. of copper when pure.

Tenorite, *black oxide of copper* (CuO), occurs extensively in Chili and Australia, etc. It is generally very impure.

Malachite is a hydrated carbonate of emerald green colour, of the composition $CuCO_3,CuH_2O_2$. It is often beautifully variegated, and is used for ornamental purposes. It occurs in Siberia, Australia, the United States, etc. It contains 58 per cent. of copper.

Azurite, *Blue Malachite,* or *Chessylite* ($2CuCO_3,CuH_2O_2$), is of a deep blue colour, and generally occurs with green malachite. An extensive deposit formerly existed at Chessy in France. It contains about 55 per cent. of copper.

Chrysocolla and Dioptase are hydrated silicates of copper. The former is blue and the latter green in colour. They contain about 30 per cent. of copper.

Redruthite, *chalcosite, copper glance* (Cu_2S), occurs native in Cornwall and elsewhere. It has a semi-metallic white appearance, and is readily scratched with a knife. It contains 80 per cent. of copper.

Erubescite, *Bornite, horseflesh ore* ($3Cu_2S,Fe_2S_3$), occurs extensively in South Africa, Australia, and Norway. It consists of copper and iron sulphides, containing up to 62 per cent. of copper. Its colour varies from copper red to pinch-beck brown, with a blue tarnish.

Copper Pyrites, *chalcopyrite, yellow copper ore* (Cu_2S,Fe_2S_3), is distinguished by its golden yellow metallic appearance. It is softer than iron pyrites, and can be scratched with a knife. When pure it contains 34·6 per cent. of copper, 30·5 iron, 34·9 sulphur. Usually, however, it is mixed with a large excess of iron pyrites (FeS_2), and does not contain more than 12 per cent. of copper, and often less. It is the principal ore of copper, and occurs in Cornwall and Devonshire, also in Siberia, in Sweden at Fahlun, in the Hartz, and various localities in the United States.

Peacock Copper Ore is a variegated copper pyrites, but is usually richer in copper.

Grey Copper Ore, *tetrahedrite, Fahl ere,* consists of sulphantimonides and sulpharsenides of copper and iron. It often contains silver, mercury, and sometimes gold. The amount of copper varies up to 38·6 per cent. It occurs extensively in the Hartz Mountains, at Kremnitz in Hungary, at Frieberg in Saxony, Kapnuik in Transylvania, and in Chili. It is worked for copper and also for silver.

Atacamite is a natural oxychloride, occurring extensively in Atacama in Chili, in Australia, and elsewhere. It is a deep green in colour.

Cupreous Iron Pyrites.—Besides the above, much copper is extracted from the cinders obtained in the burning of cupreous iron pyrites for the manufacture of sulphuric acid.

Dressing Copper Ores.—The low specific gravity of the oxidised ores of copper, and the brittleness of others, especially the sulphides, render the mechanical dressing of copper ores by wet methods difficult and involves heavy losses. In some cases the recovery of the mineral may fall below 60 per cent. of that present, with a corresponding loss of copper.

Magnetic concentration is in most cases quite impossible.

Flotation methods have been successfully applied to sulphide ores. Fig. 33 shows a froth flotation plant. (See p. 38.)

Ores as received for smelting may contain not more than 3 to 4 per cent. of copper.

Copper Extraction.

The varied character of the ores and, in many cases also, the low percentage of copper present tend to make the processes for the complete recovery of the metal somewhat complicated. The direct reduction of oxidised ores, which should be a simple matter, is rendered difficult owing to the ease with which cuprous silicate forms and the difficulty of completely reducing it. Further, the various ores generally occur in close association, and the process must be capable of absorbing them as part of the original material of the furnace charge or permit of their introduction at a suitable point in the process. The same remark applies to the slags carrying copper produced at different stages in the smelting campaign.

These difficulties led to the evolution of the original Welsh process of copper smelting, now almost superseded. It established the basis, still universally followed, of converting all the copper present in the ore in whatever form, oxides and carbonates and silicates included, into cuprous sulphide, which, in admixture with iron sulphide present in the melt, formed a regulus containing all the copper, accompanied by a slag consisting mainly of iron and other silicates.

The concentration of the copper from oxides and ores containing copper in oxidised form depends on the fact that, owing to the great affinity of copper for sulphur, oxide of copper decomposes sulphide

of iron, and the oxide of iron formed combines with silica and passes into the slag as silicate.

$$2FeS + 2Cu_2O + SiO_2 = 2Cu_2S + 2FeO.SiO_2$$

Lime may be employed to lower the melting-point and also the specific gravity of the slag. Such a slag has no solvent action on the sulphide formed, and they therefore separate in different layers. Small particles of regulus may be carried off mechanically, and a slag rich in iron oxide may dissolve a trace of regulus. The degree of fluidity also affects the amount of regulus carried into the slag. Obviously, since the main source of loss is mechanical, the loss in copper will be least with a poor regulus and increase in proportion. Slags from the production of poor regulus are therefore usually " clean," but those from rich regulus may require remelting with other charges producing poorer regulus.

From these considerations it will be seen that if a sufficient amount of sulphur—usually as iron sulphide—be present, it will be possible under ordinary smelting conditions, making a siliceous slag, to concentrate the whole of the copper until practically pure cuprous sulphide is reached, iron and other metals being eliminated by oxidation and a subsequent fluxing fusion. Oxidised copper-bearing materials can be introduced into the fusions to supplement the oxide of copper in the calcined material, hastening the enrichment of the regulus and recovering the copper contained in them at the same time. Finally, advantage is taken of the reaction between the oxides and sulphide of copper (see p. 215) to separate the metal from the rich regulus, and the copper obtained is refined and toughened. This is the basis of all methods of extraction, but the method of application and appliances used differ. In the Welsh process the operations are carried out in reverberatory furnaces, the various stages constituting separate operations, while in the modern blast-furnace methods followed by Bessemerising the number of distinct operations is minimised—oxidation, fluxing, and reduction may be effected in the same operation.

Treatment of Sulphides with air without the Addition of " Oxidised Ores of Copper."

Reaction Process.—Sulphide ores, with the exception of copper glance, do not usually contain sufficient copper to permit of its direct extraction, and undergo a series of operations, the object of which is to concentrate the copper in a rich regulus. The ore is subjected to a series of calcinations alternating with fusions in a *reducing* atmosphere. In the calcining processes sulphur and arsenic are oxidised and removed as sulphur dioxide (SO_2) and arsenious oxide (As_4O_6) respectively, and the iron and copper are partly oxidised.

$$\left\{\begin{array}{l} Cu_2S + 3O = Cu_2O + SO_2 \\ Fe_2S_3 + 9O = Fe_2O_3 + 3SO_2 \\ FeS_2 + O_2 = FeS + SO_2 \end{array}\right.$$

In the fusions which follow, the reaction of the oxide of copper on the remaining sulphide of iron produces sulphide of copper and oxide of iron. At the same time, many impurities are removed. The iron oxide thus produced, together with that formed during roasting, is removed by combining with silica, to form silicate of iron, which constitutes the slag. There is always sufficient silica in the charge and furnace bottom to effect this.

$$2Cu_2O + 2FeS + SiO_2 = 2Cu_2S + 2FeO.SiO_2$$
$$Fe_2O_3 + CO + SiO_2 = 2FeO.SiO_2 + CO_2$$

The sulphide of copper and unaltered iron sulphide fuse and form a bottom layer in the furnace. This treatment is repeated until the iron has been practically removed, and the regulus is then treated for copper by roasting and fusion, and afterwards refined. Oxidised ores and the slags produced in the fusions, which contain too much copper to throw away, are introduced into the fusions, and, by reaction on the sulphide of iron, the copper they contain passes into and enriches the regulus.

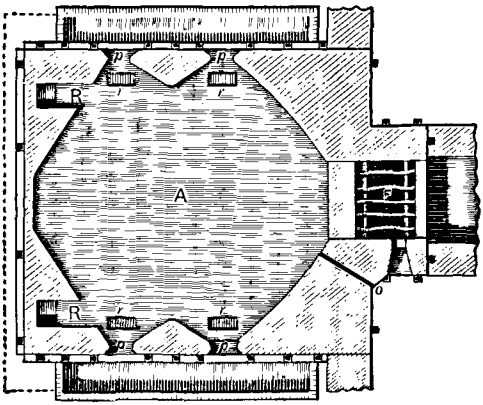


FIG. 113.—Plan of bed of calcining furnace. A, bed; F, fireplace; *p*, doors; *r*, openings into vault.

The earlier stages of this process have been entirely superseded, but the later stages survive to a limited extent. Furnace refining and poling are still carried out in the same way.

Welsh Process.—This was conducted in reverberatory furnaces throughout. The ore mixture contains from 9 to 13 per cent. of copper as sulphide, with excess of iron pyrites and silica, and the process involves at least six operations—

(*a*) Calcining the ore;
(*b*) Fusion of the calcined material with oxidised ores and slag;
(*c*) Calcining the regulus obtained in *b*;
(*d*) Fusion of calcined regulus with slags;
(*e*) Roasting and fusion of regulus with separation of blister copper;
(*f*) Refining and toughening.

(*a*) **Calcining the Ore.**—This was conducted in a reverberatory furnace, the bed of which is shown in Fig. 113. The temperature is low. About half the sulphur is removed mainly as sulphur dioxide (SO_2). Some sulphur trioxide is also evolved. Arsenic passes off as

As_4O_6. This roasting on 3-ton charges occupied about 24 hours. The roasted ore was raked into the vault below, to cool.

(*b*) **Fusion for "Coarse" Metal.**—The roasted ore was mixed with oxidised ores and slags, the charge being made up as follows :

Roasted ore, 60 to 66 per cent.
Oxidised ores, 10 to 14 per cent.
Metal-furnace slag from fourth operation, 22 to 25 per cent.

This was introduced in charges of about 25 cwts. into the "ore furnace" (Fig. 114), also a reverberatory furnace, working at a higher temperature. The bed was of sand, and sloped from all points towards the tapping hole B, under the door C in front of the furnace. As the charge fused, the oxides, sulphides, and sulphates reacted as described,

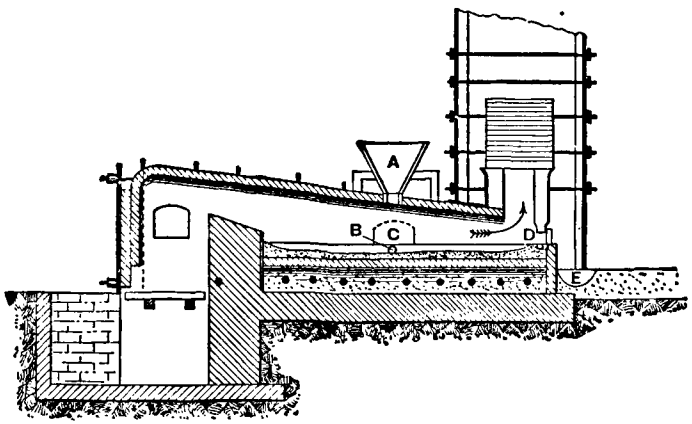


FIG. 114.—Ore furnace.

and the regulus formed separated. The slag—*ore-furnace slag*—often contained unfused masses of quartz and stony matters occurring in the ore, and was raked off the surface of the regulus through a long low opening, D, at the flue end of the furnace into sand moulds, E, beneath. Before tapping, three charges were generally fused, and the whole of the regulus run out together into sand moulds.

The metal-furnace slag—sharp slag—which formed part of the furnace charge, contained about 4 per cent. of copper as silicate, etc.

It is essential that the furnace charge should contain an excess of sulphide of iron to ensure the complete decomposition of the oxide of copper in the roasted material and in the oxides, carbonates, slags, etc., added.

The regulus obtained consisted essentially of a mixture of iron and copper sulphides, containing 30 to 35 Cu, 30 Fe, 28 S, with small quantities of arsenic, bismuth, lead, antimony, and sometimes tin, nickel, and cobalt sulphides. It is known as "coarse metal," and breaks with a coarsely granular fracture of a bronze-purple colour.

The slag is known as "*ore-furnace slag*," and consists principally of silicate of iron, and contained less than 1 per cent. of copper.

(*c*) **Calcining Coarse Metal.**—The pigs of coarse metal were crushed, unless it had been granulated, and the regulus roasted in the calciner for 24 hours at a low red heat, losing about one-half its sulphur, mainly as sulphur dioxide.

(*d*) **Fusion for "Fine" Metal.**[1]—The calcined coarse metal was mixed with roaster and refinery slags (slags from the fifth and sixth operations, containing a large proportion of cuprous oxide as silicate), and also sometimes with pure oxide and carbonate ores.

The mixture contained—

Roasted regulus, 65 to 80 per cent.

Slag and oxidised ores, 20 to 35 per cent.

The "metal furnace" in which the fusion was effected is similar to that employed in the fusion for "coarse metal." The charge consisted of about 30 cwts., and its fusion occupied from 6 to 8 hours. The same reactions between the sulphides and oxides in the charge occurred as before.

The second calcination and fusion have for their object the production of a rich regulus as free as possible from iron. The extent to which this has been accomplished depends on the efficiency of the roasting and the amount of oxidised cupreous materials added. If the oxide of copper is insufficient to decompose the sulphide of iron present, a regulus, which breaks with a smooth, shining fracture and a bluish colour, containing from 55 to 66 per cent. of copper, known as "*blue metal*," resulted. It is a mixture of cuprous and iron sulphides.

When the oxide of copper is in the required proportion, a regulus which breaks with a semi-metallic, greyish-white, slightly granular fracture, known as "*white metal*," is produced. It contains from 70 to 78 per cent. of copper, and is practically "cuprous sulphide," Cu_2S. "*Pimple metal*" contains a larger percentage of copper, and is produced when the oxide of copper is in excess.

Sometimes the oxide is in excess of requirements, in which case it reacts on the sulphide during fusion, and metallic copper is produced with an evolution of SO_2. The regulus appears to dissolve a certain amount of the reduced copper, which separates out, as the metal cools, in fine, velvety filaments, lining cavities in the metal, and is known as "*moss copper*." Separated copper is also found in blue metal, but is absent in pure white metal.

"*Metal-furnace slag*," "*Sharp slag*," has a bluish, lustrous, semi-crystalline fracture. It is essentially silicate of iron, but contains about 4 per cent. of copper, which is recovered in the second operation.

(*e*) **The Roaster Stage.**—The pigs of fine metal are placed on the bed of the roaster furnace, which in most respects resembles the metal furnace, but is, however, provided with openings at the fire-bridge, for the admission of air into the furnace chamber, and a basin-shaped depression in front of the door. The temperature is so

[1] This process is still in use to a limited extent.

managed that the melting down occupies from 6 to 8 hours. Extensive oxidation takes place, sulphur passing off as sulphur dioxide; thus—

$$Cu_2S + 3O = Cu_2O + SO_2$$

When melted, the slag which has formed is skimmed off, and the clear surface presents a boiling appearance, and emits a frizzling sound, due to the escape of SO_2 formed by the oxide reacting on the sulphide.

$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$

Metallic copper separates and sinks to the bottom of the bath. When the process is judged complete, the slag is again skimmed off and the copper tapped into sand moulds. The length of time occupied varies from 12 to 24 hours, being longest when the fine metal is least pure.

The "*blister copper*" is dry and unmalleable, has a dull red fracture, and contains cavities. The surface presents a blistered appearance, caused by sulphur dioxide liberated during solidification; hence the name. It contains about 98 per cent. of copper and less than 1 per cent. of iron.

Roaster slag has a purplish red colour, and contains from 17 to 40 per cent. of copper, as silicate and metal, according to circumstances.

Direct Process.—At Briton Ferry, working with ores of special purity, the "roaster stage" was conducted in a totally different fashion from that generally prevalent. A portion of the fine metal was roasted "sweet" in a calciner of the revolving type (Fig. 113), and mixed with a sufficient amount of the unroasted regulus—determined by experiment—to reduce it. The mixture was then heated to fusion in a reverberatory furnace. A much greater yield of copper was obtained in this way, and its quality is said to be in no way inferior. The copper was refined in the same furnace.

(*f*) **Refining and Toughening.**—The refining furnace has a sand bottom, which inclines from all parts to a basin-shaped cavity near the end door. There is also no charging hopper or tap-hole. Some 6 to 20 tons of pigs of blister copper are piled up on the bed, and gradually melted. This occupies from 4 to 6 hours. The slag is skimmed off, and the surface exposed to the oxidising atmosphere for from 10 to 15 hours longer. A temperature of about 1200° C. is maintained. Copper being less oxidisable than the impurities present, viz. arsenic, sulphur, iron, tin, nickel, cobalt, manganese, bismuth, antimony, and lead, these are removed as oxides. The solubility of cuprous oxide (Cu_2O) in the metal also carries oxygen to the impurities; but much copper, owing to its great excess, is also oxidised, forming cuprous oxide. This, with the other metallic oxides formed, combines with silica from the sand bottom, etc., and constitutes the slag. Some cuprous oxide is, however, retained by the metal, and renders it "dry" or "underpoled." The attainment of this state is determined by the withdrawal of samples from the

bath (see p. 207). To remedy this, the slag is again skimmed off, the surface of the copper covered with coal or anthracite, and a pole of green birch or oak wood is plunged into the metal and held down. The hot metal causes a copious evolution of steam and reducing gases, which thoroughly agitate the metal, bringing every portion of it into contact with the carbonaceous matter covering it, whereby the cuprous oxide in the metal is reduced. Samples are taken from the bath from time to time, examined, and tested for toughness and malleability. Microscopic examination is also made. When the metal has lost its dark-red, granular fracture, and breaks with a flesh-coloured silky lustre, bending double when placed in a vice, the "tough pitch" has been attained: the pole is withdrawn, the covering pushed aside, and the metal ladled out by hand, in clay-covered ladles, and cast into ingots weighing about 20 lbs.[1] The ingot moulds are of cast iron or copper, and so arranged that, as soon as solid, the ingots can be thrown into water. During ladling the metal is apt to become oxidised and dry again. When this is observed, the pole is reintroduced for a short time, and the metal brought back to toughness. The time occupied is about 30 hours, from introduction of pigs to end of ladling out. Oxygen should be below 0·1 per cent.

In modern copper refining soda and soda ash are added during the oxidising stage to combine with and remove the oxides of arsenic and antimony, and the reduction of the excess oxide of copper in the bath is more rapidly effected and the time shortened by the careful addition of powerful reducing agents in suitable amounts. Substances employed for this purpose include calcium boride and silicide, lithium, and phosphor copper. Cadmium is also used. Slight excess of the latter metal does not seriously impair the conductivity and other properties of copper. In wire bar from 0·5 to 2 per cent. is sometimes present.

The final poling follows.

Schumacker states that copper containing 0·18 residual calcium has a conductivity of 97·5 per cent. With similar amounts of silicon and aluminium the conductivity is only 86·1 per cent. Lithium is less injurious than calcium, but is more liable to introduce other impurities from refractories. He prefers a mixture of calcium boride and lithium, and obtained 101·0 per cent conductivity. 0·3 per cent. iron in completely deoxidised metal reduced conductivity to 95, but only to 100·6 if 0·005 oxygen be present.

Modern refining furnaces of much greater capacity—up to 200 tons—are now in use. The furnaces may be coal dust or oil fired and are provided with special charging and casting appliances. The copper is run from the furnace either into an iron ladle lined with refractory material or directly through an interrupter launder acting as a forehearth into the moulds. In casting large ingots for rolling the ingot moulds—copper in an iron frame—are carried on arms radially disposed round a 13 ft. hub. A mould press supplied with copper from

[1] The casting temperature is about 1125° C–1150° C.

the furnace is provided to keep up a supply of moulds. After filling the ingot moulds are cooled by water spray underneath. Each ingot is dropped automatically into a water bosch when the machine has revolved about half-way round from the pouring point. A spray gun is employed to give the surface of the mould a wash with finely ground bone ash.

Refinery slag is of a coppery-red colour. It consists mainly of silicate of copper, not infrequently with shots of metal freely dispersed through it.

"Basic" linings have been introduced in the roaster and refining furnaces. The loss of copper in the slag is much less, owing to the absence of silica, which by combining with the oxide formed in roasting retards its reaction on the sulphide. The yield of blister copper is said to be 25 per cent. more than with sand bottoms. Arsenic is removed to a greater extent, but bismuth and antimony in no greater degree than on a siliceous bottom. In refining arsenical metal, soda ash is added as well as lime.

Modifications of the Welsh Process.—In some cases, owing to poorness of the ores, or the lack of oxides and slags, or sometimes difference in practice, the number of operations was increased, the roaster stage for the production of blister copper being preceded by more calcinations and fusions, to produce a satisfactory regulus.

A small quantity of lead is often added to copper intended for rolling, just before ladling; after which the scum of oxides which forms is skimmed off. The amount added varies from 0·1 to 0·5 per cent. Its object is twofold. By its oxidation it promotes the oxidation and removal of foreign metals present, notably antimony, and also retards the metal from "going back" by oxidation, and again becoming dry and underpoled. The ingots are sounder and flatter. Copper containing not more than 0·1 per cent. of lead rolls well, and has a less tendency to collar the rolls. It is a little more difficult to detach the scale. No addition of lead is made in making best selected copper, or copper intended for making best brass, gun-metal, or German silver.

"Best selected" copper was formerly made from the purer portions of the "fine metal" resulting from the smelting of purer ores. It is found that the impurities become concentrated by gravity in the lowest part of the bath, and consequently those pigs which flow from the furnace first are most impure. The selection of the later ones for making the best copper led to the introduction of the term. Best selected copper should contain only traces of arsenic, antimony, and bismuth.

Another process of selection followed was known as the "bottoms" process. In this process the "fine metal" obtained in the fourth stage, prior to tapping, was cleared of slag and roasted. The oxide of copper formed reacts on the sulphide, and copper is reduced. This attacks the foreign sulphides, reduces them, and alloys with the liberated metal, thus concentrating them in the metallic state, and carrying them to the bottom of the bath. This leaves the "fine" metal purified. The "bottoms" copper contains nearly all the gold and silver, and much of the tin, lead, and antimony in the charge.

BOTTOMS COPPER.

	Percentage of elements removed from blister.
Antimony	80·8
Tin	93·4
Bismuth	47·6
Arsenic	60·2
Gold	All
Silver	42·9

Instead of employing reverberatory furnaces exclusively, blast furnaces of the "water-jacketed" type are now commonly used for the fusion of ore and regulus.

Reduction Processes.—Oxides, carbonates, and other oxidised copper ores, if in sufficient quantity, may be smelted in blast furnaces—preferably water-jacketed—with coke and a suitable flux, *e.g.* oxide of iron, to slag off silica. By adding a little iron pyrites to the charge, a small amount of copper regulus is formed, as well as metallic copper, and the slags are cleaned.

Sulphide of copper is not completely reduced by iron or carbon. It is necessary, therefore, to convert "mattes" into oxide, before reduction, by calcining. They may then be treated as above. This is also done with the "fine regulus" obtained at Mansfeldt in Germany, where the regulus is desilverised by the Ziervogel process (p. 278). The finely divided residue of oxide of copper and iron is balled with a little clay and smelted for "black" copper, which is afterwards refined by oxidation by an air blast on a small hemispherical hearth, under charcoal.

General considerations of Modern Methods.—The location and working of enormous deposits of ore of a generally uniform character has led to revolution in methods of copper smelting. These deposits often occur in wild, out-of-the-way places. Smelting methods which economise fuel and labour are essential in remote districts where coke often had to be transported very long distances by men. Output has also to be considered in connection with overhead charges. The Welsh process was efficient but costly, and the output restricted.

Modern methods, while depending on the same basic principles, are carried out in a manner which reduces the number of operations to the smallest possible, economises fuel, and enables large quantities of material to be dealt with. They involve :—

(1) A preliminary roasting (for sulphide ores) to eliminate excess of sulphur and oxidise metal.
(2) A fusion for matte to concentrate copper and other metals, carried out in blast or huge reverberatory furnace.
(3) Bessemerising the regulus for blister copper.
(4) Refining by fire-methods or electrolytically (followed by fusion of the copper).

Since the available sulphur in the charge combines with copper and iron during melting, the amount of matte produced in the fusions

will depend on the percentage of that element remaining in the ore after calcination or present in the furnace charge when smelted.

In order to produce a matte sufficiently rich for further treatment the sulphur must be carefully controlled in the calcination and sub-

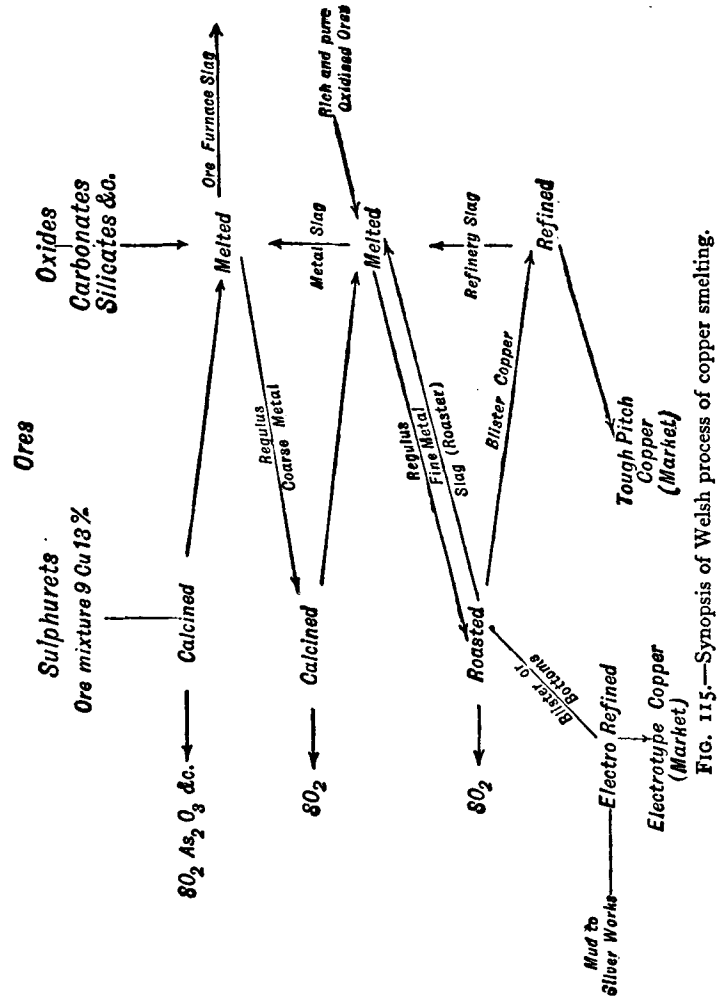


FIG. 115.—Synopsis of Welsh process of copper smelting.

sequent mixing of ores and products (slags, etc.) which constitute the charge. The ratio of the volume of matte to slag must be considered in the light of the richness of the ore. With poor ores, poor mattes and fusible slags must be produced, in order to make the volume of mattes sufficient to collect the copper, and the slag sufficiently fluid to allow of its complete subsidence in the furnace or forehearth. In any

case fusibility and fluidity of slag must be ensured to prevent matte being carried away in shots mechanically. Regulus usually containing from 28 to 50 per cent. of copper is produced.

Melting is carried out in water jacketed blast furnaces or in reverberatory furnaces, often oil or dust fuel fired.

In either case the composition of the smelting charge is carefully adjusted. Ore (calcined and raw oxidised ores), copper-bearing slags, and other materials are mixed with care.

For smelting in blast furnaces the material must not pack so tightly as to prevent passage of the fire gases, and so lead to the formation of obstructions due to absence of sufficient heat carried by the gases. The presence of the admixed coke helps to keep the charge open.

For reverberatory smelting fines are not objectionable and permit of more perfect mixing.

In melting, especially where electrolytic refining is employed, ores containing little copper but carrying gold values may be added to the mixture to recover the precious metal.

Bessemerising of the matte combines all further treatment to the point of producing blister copper on both poor and rich mattes, the practice varying with quality and other circumstances. The chemical changes take place in the same order as in the old methods. The sulphur and iron in the iron sulphide are eliminated partly by direct oxidation and partly by reaction with oxide of copper also produced by the air blown in. The oxide of iron formed passes into the slag.

$$2FeS + 3O_2 + SiO_2 = 2FeOSiO_2 + 2SO_2$$
$$FeS + Cu_2O = Cu_2S + FeO$$

The perfect admixture of the molten material ensures that the oxide of copper comes into contact and reacts with iron sulphide before it can combine with silica or slag-forming materials and pass into the slag.

When the iron sulphide has been removed, the copper sulphide remaining is reduced by the interaction of oxide and sulphide of copper, as shown on p. 215. The heat required in Bessemerising is produced by the oxidation of iron and sulphur.

Refining methods will be governed by working conditions and composition of matte. Electrolytic refining is generally followed for blister copper containing gold and silver or nickel, but is practised for all types of blister.

Fire refining is still largely followed. It may precede electrolytic refining in some cases where the blister is very impure.

It follows the usual lines already dealt with, but modern refinery furnaces are much bigger (up to 200 tons), and may be fired with oil or coal dust and provided with an air blast sufficiently strong to blow aside a slag covering to reach the surface of the metal for oxidation purposes.

Electro-deposited copper—cathodes—are melted and toughened before casting into ingots.

A rectangular water-jacketed furnace is shown in Fig. 116. Such furnaces are limited in height owing to the charge often containing much fine material, and to the necessity of avoiding reduction of the iron oxide flux, to metal or magnetic oxide. See p. 247.

The charge consists of a mixture of calcined and raw ores, and materials so apportioned as to require the least addition of the necessary fluxing materials Oxide of iron and limestone constitute the fluxes, but if silica be deficient it must be added.

The slag is a double silicate of lime and ferrous oxide, containing—

Silica	. .	32–45 per cent.
Oxide of iron		24–35 „
Lime	. .	25–33 „

It is allowed to flow continuously from the slag notch into a receiver or catch-pot, from which it overflows into slag pots which are removed when full.

The slag flowing from the furnace just below the fusion zone carries fine globules of regulus with it. These settle in the catch-pot which is replaced from time to time and the slag solidifies. (See p. 245, Fig. 122.) When the block of slag in the pot is turned out a large conical lump of regulus is found. This is broken off.

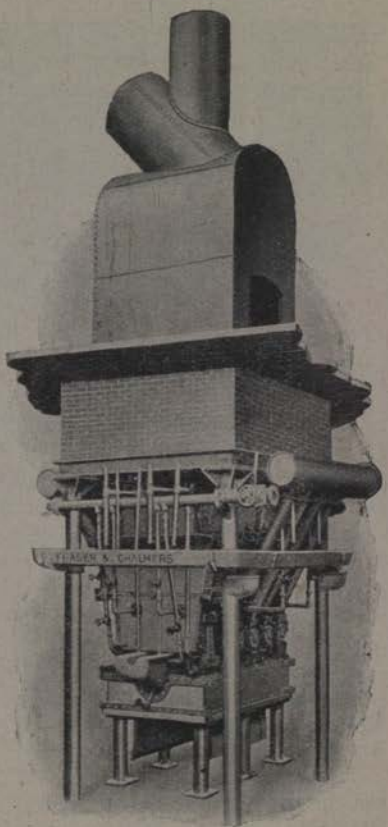


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FIG. 116.—Rectangular water-jacketed furnace.

The regulus may be removed from the furnace at intervals. In many cases the fused regulus and slag flow from a common opening into a receiver, in which they separate, the slag flowing over a slag notch, and the regulus being tapped as necessary. Fig. 117 shows such a movable receiver.

The treatment of fine ores in blast furnaces has always been difficult. With modern methods of concentration, *e.g.* flotation, these difficulties are increased.

Briquetting has been followed, but there is always a liability for

the briquettes to fall to pieces and crumble in the upper part of the furnace and choke the draught. Methods for agglomerating fine ore by sintering processes more or less resembling those described for lead (p. 245) are now being rapidly extended. The fine material is "pot" roasted either in the raw state or more generally after partial roasting. By this treatment it is converted, more or less completely, into a hard clinker suitable for blast-furnace treatment.

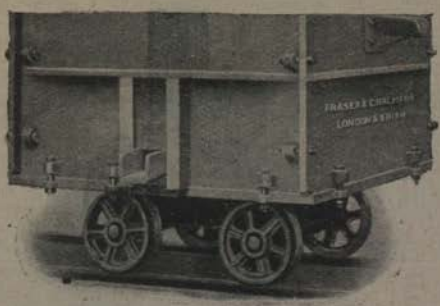

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FIG. 117.—Movable receiver or forehearth.

The rapid development of high-dressing processes, producing so large a proportion of very fine material, has led to a reversion to reverberatory furnace methods for matting.

Matte Smelting in Reverberatory Furnaces.—Fine ores are unsuitable for blast-furnace treatment. They prevent the proper distribution of the gases and heat, thus causing the charge to "hang" in the furnace. Much loss also arises from the fine material being blown out of the furnace.

Large reverberatory furnaces are preferable for the treatment of such ores, where large amounts of similar material, adequate fuel supplies, and favourable labour conditions exist. Figs. 118 and 119 show a large oil-fired modern reverberatory furnace for matting fine ores.

In coal-fired furnaces the ratio of grate area to bed is as 1 : 16. Long-flaming bituminous coal is used. Coal-dust fuel (approximately 100-mesh fine) and producer gas are also in use for heating copper-smelting reverberatories.

The main working difficulties in matting in reverberatory furnaces are the maintenance of the banks of the furnace bath and control of the composition of the slag.

In smelting calcined pyrites and other ores, the oxide of iron which has to be fluxed causes the sand banking to be rapidly attacked and to require frequent repair. In earlier furnaces of the same type openings were provided in the roof of the furnace along the sides through which sand to replace that fluxed could be let down. The control of the slag is difficult because at the working temperature equilibrium will be established between the basic and acidic components. In the presence of excess of silica the slag will saturate itself with that body, and increasing the basic contents of the charge only leads to an increase in the total slag, the composition of the slag remaining practically constant.

Both these evils are remedied by the introduction of banks of chromite in the furnace illustrated. The bottom is of sand, but as it is

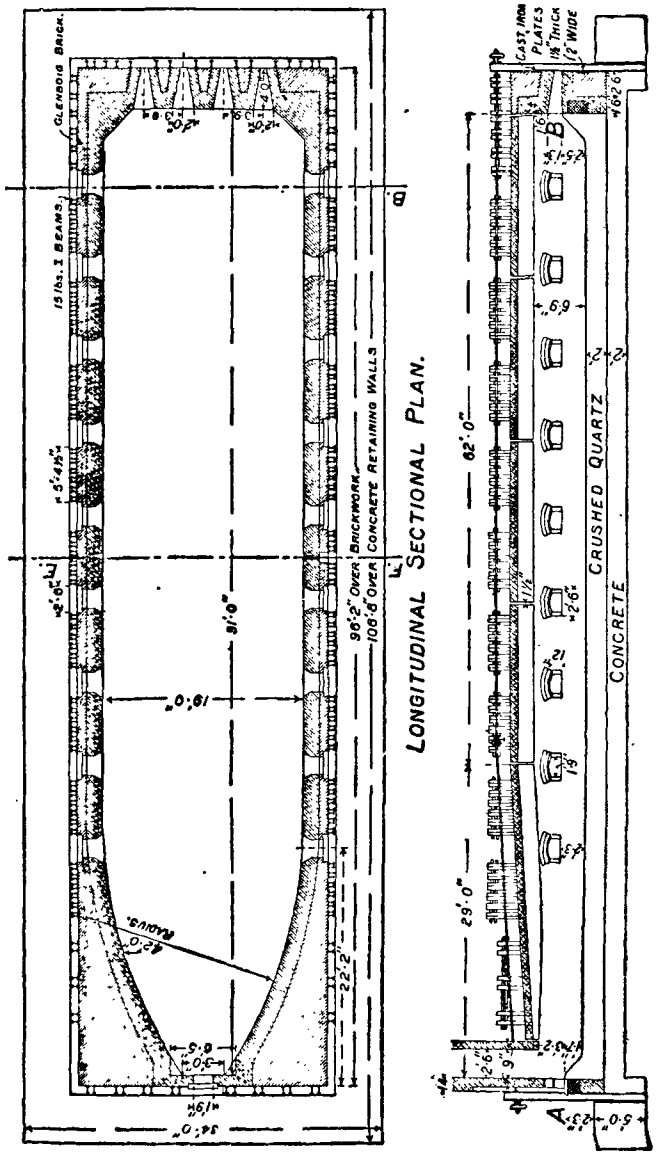

FIG. 118.—Large oil-fired reverberatory furnace for matting copper ores.

always covered with matte—the sulphides do not attack the sand—it does not suffer. The furnace is 106 feet long and 19 feet wide.

The oil burners are situated at the end usually occupied by a fireplace. The flue opens out of the roof over the skimming door as usual. It is usual to provide a stack of considerable height, but it should be remembered that in this, as in all cases where forced draught is employed, only sufficient " pull " should be maintained as will prevent the flame and hot gases escaping round the working doors and other apertures. It is essential that the hot gases shall be retained as long as possible in order that the heat may be utilised in the furnace and not wasted in the flues. Much waste occurs when this is not observed.

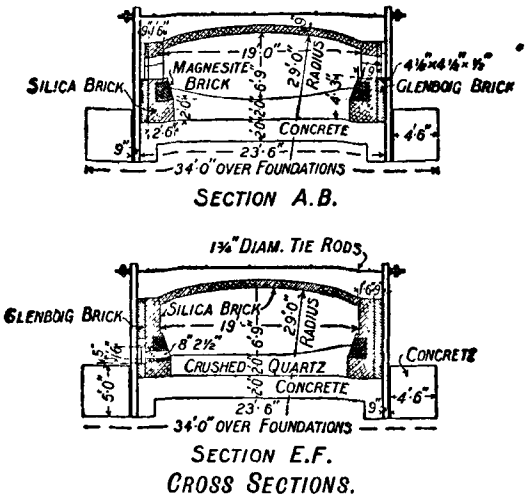

FIG. 119.—Large oil-fired reverberatory furnace.

Longitudinal and transverse sections are shown, the latter through the tapping hole. The slag flows away at the skimming door end of the furnace. In recently erected furnaces the charging hoppers are confined to the firing end, the charge being let down through holes in the roof. This secures a long run for the slag before it passes from the furnace and gives opportunity for perfect separation of slag and matte to take place.

The furnace has a capacity of 400 tons per day.

The original oil furnaces of this type were erected at Cananea, but their use has extended owing to the ease attending the use of oil fuel.

Further improvements have been introduced. The charge is admitted by openings in the roof at the sides, and itself protects the banks of the furnace, further supplies falling down as the melting proceeds.

In the latest American plants direct smelting of the wet ore-concentrates with Bessemer slags and Cottrell dust and the necessary fluxes is being introduced. This eliminates the roasting process and greatly reduces the dust problem.

For this furnace the charge is mixed to produce slag of a composition

that, while being fluid and clean, is the smallest possible quantity that can be secured with free working. Limestone is used as a source of lime, but generally the necessary oxide of iron and silica are present in the ore, or may be introduced by mixing suitable ores, some of which while carrying little copper, are stripped in the process. The fluxes are sometimes added prior to calcination.

The composition of the slag varies from 30–45 per cent. silica, 25–35 per cent. oxide of iron, 10–25 per cent. lime, 0·3–0·4 per cent. copper.

Pyritic Smelting.—As already pointed out (p. 66), sulphur is a valuable source of heat. Compared on the basis of the amount of heat given out when combining with equal amounts of oxygen, in which case the same volume of nitrogen will have to be considered, the comparison with carbon is as follows :—

$$C + O = CO + 29{,}676$$

$$C + O_2 = CO_2 + 96{,}960$$

$$S + O_2 = SO_2 + 72{,}350$$

For sixteen parts of oxygen the figures become 29,676, 48,480, 36,175 respectively. Since the volumes of gas produced by carbon burning to carbon dioxide, CO_2, and sulphur to sulphur dioxide, SO_2, are the same, and both are volatile products, the figures represent approximately their relative heating values when air is conducted to an excess of the material. Obviously, if the sulphur be burnt under proper conditions ores rich in sulphur should produce sufficient heat to melt the products—matte and slag.

The nature of the ore and its fusibility offer points of difficulty in continuous working. It is necessary that the ore should contain sufficient sulphur to supply heat and sufficient free silica to flux the oxide of iron produced. A type of blast furnace is used.

Ores containing a minimum of 18 per cent. sulphur corresponding to 28–30 per cent. pyrites, may be treated in this way.

Briefly the method is as follows : The furnace is started with a wood fire, the elongated form of the timber facilitating the flow of gases, and the ore is charged in, a large blast being maintained. The sulphur burns and calcination and fusion take place in the same furnace, the degree of concentration depending largely on the rate of fusion. If the fusion takes place too readily the iron may not have been oxidised and removed, and a low-grade matte will result. Where this is likely to occur partial calcination or admixture with other ores is effected prior to smelting. In order to keep the furnace working it may be necessary to use a little timber or other fuel from time to time. The amount of coke so used varies from 2–4 per cent.

The products of the furnace are matte and slag. The matte contains from 20 to 28 per cent. of copper, and the slag is mainly ferrous silicate.

At Mount Lyell the ore treated contains 2·15 to 2·25 per cent. of copper. During the process 95 to 96 per cent. of the iron is oxidised and a matte containing 35 to 45 per cent. of copper obtained. A blast of 4 lbs. pressure is maintained on the furnace, in which the height of the ore column is 18 feet. Unheated air and a large volume at high pressure have been found to yield the best results.

The slag contains 36 to 38 per cent. silica, 45 per cent. ferrous oxide, some lime, and about 7 per cent. alumina. As noted under Lead, the amount of alumina in such slags should not exceed 10 per cent. The slag contains from 0·35 to 0·45 per cent. copper.

At Mount Lyell the concentration is approximately 20–1, a very high ratio. With a lower concentration cleaner slag can be produced.

Treatment of Matte.—In large works the recovery of copper from matte is effected now almost entirely by Bessemerising, but a minimum daily output of about 30 tons of copper is necessary for efficiency. The principles underlying the treatment of copper matte are: When air is blown through molten matte the iron and sulphur are first removed. A series of chemical changes are taking place side by side. The sulphides are oxidised, sulphur passing off as sulphur dioxide, and any oxide of copper produced immediately reacts with iron sulphide, producing more oxide of iron and reconverting the copper into sulphide. This continues until all the iron sulphide has been oxidised. The iron oxide is fluxed by silica, forming iron silicate, and practically pure copper (cuprous) sulphide remains.

If the blowing be continued the oxidation of the sulphur proceeds, and the reaction between oxide and sulphide liberates the copper. If prolonged the copper itself oxidises.

The whole of the changes necessary to produce rich matte and blister copper are therefore concentrated in one operation.

It will be seen that much iron oxide will be produced in the earlier stages of the blow, and that to remove it silica flux will be required. In the earlier days of copper Bessemerising the lining of the converters was siliceous and made specially thick to supply the silica necessary. This entailed rapid corrosion and frequent repair of the lining. Basic linings are now substituted and silica is added for fluxing purposes during the operation.

Both upright and barrel-shaped converters are used. Formerly small converters were used, but the development of basic linings has necessitated a large increase in size in order that the body of metal in the converter shall contain sufficient heat to avoid chilling when silica is added for fluxing purposes. The Bisbee type of Bessemer converter consists of a cylindrical or barrel-shaped vessel capable of revolution on riding rings, resting on rollers, by means of rack and pinion gearing. Such converters vary in length from 10 to 20 feet, and 7 to 11 feet in diameter. The vessel can be lifted clear of the stand and another put in place when repairs are necessary. Upright converters are also used. (Fig. 120.)

The blast is conveyed to the wind box at the back of the converter through the hollow trunnion, and the vessel can be revolved so as to bring the tuyères to any desired level below the surface of the matte. This provides for adjustment to suit the varying level of matte arising from the diminution in amount as the operation proceeds or the enlarged capacity of the vessel which results in acid-lined vessels from the fluxing of the silica lining. When silica materials are used it is the practice to make the lining as thick as possible in order to prolong the life of the vessel. The tuyères are half-inch holes through the lining. When blowing it is necessary to keep them open by punching

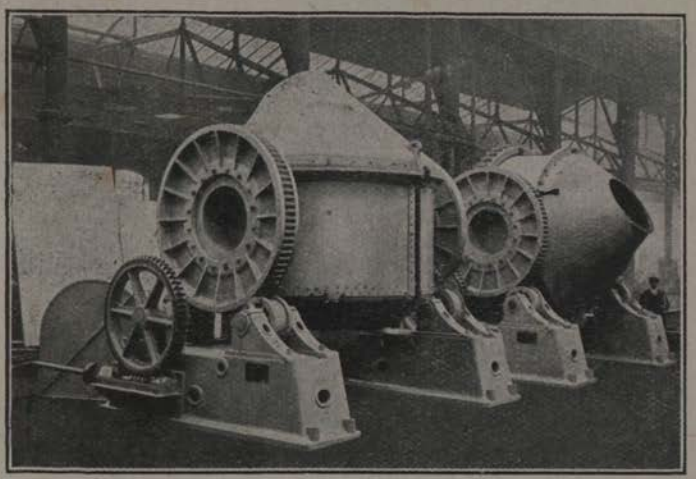

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FIG. 120.—Two electrically tilted copper converters.

with an iron rod. When blowing the tuyères are adjusted so as to be some distance below the level of the matte but to leave ample room below the tuyère level for the enriched matte or separated copper, as the case may be, to accumulate below the action of the blast, until the end of the operation approaches.

The lining of crushed quartz with sufficient clay to bind it—or similar material—is introduced round a core. The body lining has an initial thickness of 2 feet or over, but this tapers to about 6 inches at the neck, which is lined separately and attached afterwards. The whole lining is dried and heated. This takes about 24 hours. Molten slag is sometimes used for drying. It saves fuel and time. In many cases where a siliceous lining is used the vessel is first lined with magnesia bricks as a permanent backing.

An acid-lined converter, 8 feet diameter and 11 feet long, will weigh when lined about 24 to 25 tons, including some 14 to 15 tons of lining material, and will last about three or four blows on 50-per-cent.

matte, producing about 15 tons of blister copper before repairs or relining is necessary.

Blowing the Charge.—The converter is rolled on its side with the tuyères up and the matte run in from a ladle. Blast, at pressures varying from 8 to 16 lbs. per square inch, is turned on, and the vessel turned into a position which brings the tuyères to deliver the air well below the surface of the matte. Rich matte, containing 50 per cent. copper, can be blown to blister copper at one operation. Poor matte must be raised to this percentage by a preliminary treatment. Two methods may be followed. Low-grade matte containing more than 20 per cent. copper may be concentrated to 50 per cent., and the rich regulus run from the converter into moulds, and, after remelting at a high temperature in a cupola, returned to the same converter or to another reserved for treating rich matte and producing blister copper. The only real objects gained are the possibility of judging the end of the operation more certainly owing to the maintenance of conditions over a longer period, due to the capacity of the converter being less variable as the result of removal of the silica lining by oxide of iron, and the assurance of sufficient heat to complete the operation without freezing. The temperature at the beginning of the blow is approximately 1100–1150° C., at the end approximately 1250°–1300° C.

The method more commonly followed is to follow up a charge of poor matte by further additions till the converter contains a full charge of rich matte, run off the slag, and proceed to blow to blister copper without removal from the converter. With facilities for adjusting the height of the tuyères, this, it will be seen, is possible.

The Blow.—There are no definite indications of the end of the blow such as the drop of the flame in the steel processes, and much judgment is necessary to complete the removal of the sulphur without overblowing the copper.

In blowing low-grade to high-grade matte, the earlier stages of the blow are marked by the evolution of dense white fumes, consisting of the oxides of volatile metals, and sulphur dioxide, probably with some sulphur trioxide. As the operation progresses, the flame becomes greenish, and this is sometimes succeeded by a blue and rosy colour, and much practice and skill are required to enable the workman to decide when the operation has reached the desired stage. Some indication is obtained from the material clinging to the rod used in punching out the tuyères in both the first and second stages of the blow.

In the later stages—blowing rich matte to produce blister copper—the changes in flame appearance are somewhat similar. Further indication of the approach of the end—total removal of sulphur—is afforded by the behaviour of the particles of material projected from the mouth of the converter, and which impinge on an iron plate. As long as they show a tendency to stick and to glow the sulphur has not gone. When they rebound without glowing the end has been reached. (Prills of copper adhere to the converter hood.)

Basic-Lined Converters.—Owing to the interference with regular working and the cost of repairs due to the wear of a silica lining, many attempts were made to use a basic or neutral lining and supply the necessary silica by direct addition in the converter during the blow. Graphite and other linings were used and silica was conveyed in fine powder by the blast or was added at the mouth of the converter.

These attempts were not satisfactory. Many reasons contributed to the failure, but the most important was that in operating on small quantities of material in the small converters then in use there was not a sufficient body of material to retain enough heat to provide any for use in any way without cooling the charge. With a larger body of metal the heat absorbed does not produce any sensible drop in temperature, and solid silica may be added in pieces approximating to the size of walnuts for fluxing purposes.

The introduction of a basic lining removes much of the relining difficulty, since wear by fluxing does not take place. Chromite and magnesia bricks are used as linings, with or without slurry—the material in admixture with tar (see p. 60). The tuyères are made with iron pipes which burn back two or three inches into the lining when in use.

The behaviour of matte in a basic converter is very different from its behaviour in an acid-lined vessel. When poor matte is blown without the addition of silica—*i.e.* in the absence of a flux—the iron is largely converted into magnetic oxide of iron, which is infusible at the temperature and forms a coating on the lining which grows in thickness.

It is usual in putting a new converter to work to form a 3-inch coating of oxide to protect the lining. When the converter cools down the differences in expansion cause this coating to flake off more or less, and for this reason a gas supply is maintained, if possible, to keep the converter hot when temporarily out of action. By this means the lining is rendered more or less permanent. Using much silica in a poor matte blow will reduce the thickness of the coating.

$$3Fe_3O_4 + FeS + 5SiO_2 = SO_2 + 5(2FeO.SiO_2)$$

To prevent undue accumulation of magnetite with a corresponding reduction in the capacity of the converter, it is usual to produce or introduce alumina in one form or other with the matte to form a skin over the magnetite. This prevents the adhesion of other magnetite, which may form or be introduced in a matte containing it. In large works the basic-lined converters have superseded acid-lined vessels.

If the blowing be incomplete sulphur will remain in the product. Occasionally as much as 2 per cent. may remain. The metal after skimming off the slag appears black and shining. Overblown metal will appear scoriaceous and burnt. The metal is poured from the converter into iron moulds on bogies. Sometimes the metal contains a large amount of gas in solution. In this case it cools down to or below its solidifying point, and on solidification the gas is suddenly

released and throws the copper out of the mould with explosive force—gas finish.

All slags are returned to the furnace for recovery of the copper carried.

In some cases the matte is Bessemerised in the reverberatory furnace, by blowing air through the bath of melted sulphides, movable tuyères being employed for that purpose. By this means the sulphur is burnt out and iron oxidised and removed, all the reactions of calcination and fusion taking place in the fluid bath.

Electrolytic Refining.—In consequence of the great demand for pure copper for electrical work, a very large proportion of the blister copper produced by Bessemer and other furnace methods is now refined by electrolytic methods.

The crude copper is cast into thick plates,[1] which are suspended in a bath consisting of a solution of copper sulphate containing free sulphuric acid. They are connected by suitable means with the positive pole of a dynamo, constituting the anode or dissolving pole. Opposite to these, at a suitable distance, thin plates of pure copper connected with the negative pole are suspended. These form the cathode or depositing pole. The current thus passes from the crude copper through the solution to the plates of pure copper. Copper is deposited at the cathode and the acid liberated attacks and dissolves copper from the anodes, which in turn is deposited. The crude copper is gradually dissolved and deposited on the pure copper plates. By proper management of the current the impurities in the blister copper are either left undissolved, forming a mud which sinks to the bottom of the bath, or, if dissolved, are not deposited with the copper but accumulate in the electrolyte.[2] Gold and silver are not attacked, and remain in the mud, which also contains most of the lead, and other impurities. Iron passes into solution. To ensure the purity of the copper only a very low voltage can be employed. Two methods of carrying out the process are followed. In the "**multiple**" system the anodes are suspended in the electrolyte alternating with thin copper cathodes as stated above, the distance apart being 2 inches. All the anodes and all the cathodes in each tank are connected to the + and — conductors respectively. Each tank contains from twelve to thirty pairs of plates. The potential difference between each pair of plates in the same tank is the same. To reduce the voltage to the low figure necessary to secure regular working and the production of pure copper by leaving the impurities in solution, a number of tanks are connected in series. A refinery may contain 1,800 to 2,000 tanks, divided into groups. The tanks in each group are connected in series, the groups being connected in parallel. For uniform deposition it is necessary to keep the liquid circulating, and each tank in a group is placed at a slightly lower level than the one preceding it to enable liquid overflowing from one tank to pass to the next. All the end tanks of the

[1] Approximately 1½ inches thick, weighing from 200–500 lbs.

[2] Selenium and tellurium are also left in the mud.

groups drain into a common receptacle, and from this the liquor is elevated and delivered continuously to the top tank of each group. The division of tanks is necessary to keep down the voltage, and thus secure a uniform deposit as free from warty excrescences as possible.

The thin plates of copper for the anodes are made by depositing a thin layer of copper on rolled copper, the surface of which has been dressed with oil and graphite to prevent adhesion, and facilitate stripping. These are wired on to the conductors of the baths.

The electrolyte used in the refining tanks contains about 1·5 per cent. of free sulphuric acid and 5 per cent. copper sulphate. Formerly the temperature employed was 90° F., but temperatures up to 150° F. are now used.

In order to secure uniformity the current density must be carefully regulated to suit working conditions. At the lower temperature 15 to 20 amperes per square foot are a maximum, but with the higher temperature from 30 to 35 amps. may be employed, the potential drop per tank being 0·5 to 0·6 volt.

In the "**series**" method of working the crude copper is made to serve both as anode and cathode. The plates of blister copper are hung in the bath at equal distances apart, and are not connected together. It is, in fact, essential that they should be insulated except through the electrolyte. This prevents the use of lead-lined tanks. Only the end plates in the bath are connected to the poles of the dynamo. Under these conditions one side of the copper plate is positive and the other negative to those before and after it in the series. Thus one side dissolves and the other receives a deposit of copper. To prevent adherence the side receiving the deposit is coated with graphite. In this method the number of tanks and electrical connections is reduced to a minimum.

Irregular solution of the anode prevents the whole of the copper being dissolved and redeposited, and a large amount of scrap is often produced. In the multiple system the portions of the plates not immersed always form scrap—waste ends. With the series system the whole plate, except the end plates, may be immersed, and this reduces the loss from waste ends.

Note.—In addition to iron, nickel, arsenic, and antimony are wholly or partially dissolved. The two latter may accumulate and "foul" the solution. Antimony sometimes forms a basic salt which carries down the arsenic into the mud.

Slight additions of glue, oil, and other substances are often made to promote toughness and smoothness of cathode deposits.

Cathode Copper.—The deposited copper is only used as deposited in special cases. Copper is thus deposited on iron mandrils for rollers for calico printing.

All the cathode copper used for general purposes is melted in a furnace, and as a result of the oxidation requires poling.

Regeneration of Electrolyte.—The accumulation of impurities in the electrolyte tends to increase the resistance of the circuit and to the production of impure copper. To maintain it in a satisfactory

condition a portion is removed from the tank room each day and sent to the purification plant. It is concentrated by evaporation and the bulk of the copper sulphate allowed to crystallise. The mother liquor is then passed through electro-depositing tanks with lead or other insoluble anodes to remove copper and most of the arsenic and antimony. Afterwards it is either returned for re-use or further evaporated, and the iron and nickel salts crystallised out, the acid being sent back to the tank room. Or, all the copper may be electrolytically deposited by a heavy current, the liquor afterwards concentrated by evaporation, and the nickel salt crystallised out from the strong acid liquor. After settling and sand filtration the acid is used again.

Copper Slimes.—The undissolved residues contain the silver and gold which are not attacked by the sulphuric acid. They differ widely in composition.

ANALYSIS OF COPPER SLIMES.

Copper	46·84 per cent.	32·11 per cent.	45 per cent.
Gold	1·45 „	0·59 „	2·5 „
Silver	15·72 „	7·86 „	8·0 „
Arsenic	traces	3·07 „	0·12 „
Antimony		5·04 „	0·22 „
Nickel		trace	0·037 „
Selenium	0·65 „	0·12 „	24·61 „
Tellurium			3·77 „
Bismuth	0·71 „	0·07 „	
Sulphur	2·21 „	5·94 „	
Insoluble	9·68 „	1·18 „	2·18 „
Copper sulphate	— „	11·33 „	
Lead sulphate	— „	23·32 „	2·79 „
Calcium sulphate	— „	0·53 „	
Iron	— „	0·98 „	0·34 „
Manganese	— „	0·21 „	
Zinc	— „	0·14 „	SO_4 6·21 „
Not determined	22·74 „	7·51 „	4·22 „

The undetermined matter consisted of graphite, grease, and other admixed impurities.

The copper is removed from the slimes by treatment with sulphuric acid

$$Cu + H_2SO_4 + O = CuSO_4 + H_2O$$

in a lead-lined vat heated by steam coil, hot air being blown through for twelve hours. The copper, bismuth, iron, and the bulk of the arsenic are dissolved. After settling the liquor is withdrawn, and if all the copper has not dissolved, the slime is treated with silver sulphate, from the subsequent parting operations, to remove the remainder, silver being deposited in its place.

$$Cu + Ag_2SO_4 = CuSO_4 + 2Ag$$

Any excess is decomposed by a small addition of raw slimes or copper precipitate. After boiling well with water—in the same vat—the

slimes are well washed by decantation several times and filtered. They are then dried and smelted with soda ash, sand, and other fluxes in a small furnace. The dore bullion is afterwards parted. Treatment of slimes containing tellurium and selenium. See p. 284.

Wet Processes of Copper Extraction.

In wet methods of extracting copper the metal must first be converted into a soluble form, as sulphate or chloride, and the copper deposited from solution by iron or electrolytically.

Sulphate Roasting.—The conversion of the copper in pyritical ores into sulphate may be effected by careful calcining in a reverberatory furnace at a low heat. The sulphide of copper is converted into sulphate, partly by direct oxidation, thus—

$$\underset{\text{Cuprous sulphide}}{Cu_2S} + \underset{\text{Oxygen}}{5O} = \underset{\text{Copper sulphate}}{CuSO_4} + \underset{\text{Cupric oxide}}{CuO}$$

$$\text{or } \underset{\text{Cuprous sulphide}}{2Cu_2S} + \underset{\text{Oxygen}}{7O} = \underset{\text{Copper sulphate}}{CuSO_4} + \underset{\text{Cuprous oxide}}{Cu_2O} + \underset{\text{Sulphur dioxide}}{SO_2}$$

and partly by the SO_3 liberated from ferrous sulphate formed by the calcination of the iron sulphide present, or produced by the combination of oxygen with the SO_2 generated, brought about by the "contact action" of the ferric oxide and silica, and brickwork of the furnace—

$$\underset{\text{Iron pyrites}}{FeS_2} + \underset{\text{Oxygen}}{6O} = \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Sulphur dioxide}}{SO_2}$$

$$\underset{\text{Ferrous sulphate}}{2FeSO_4} + \underset{\text{Oxygen}}{O} = \underset{\text{Ferric oxide}}{Fe_2O_3} + \underset{\text{Sulphur trioxide}}{2SO_3}$$

$$\underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Oxygen}}{O} = \underset{\text{Sulphur trioxide}}{SO_3}$$

$$\underset{\text{Copper oxide}}{CuO} + \underset{\text{Sulphur trioxide}}{SO_3} = \underset{\text{Copper sulphate}}{CuSO_4}$$

Copper sulphate requires a higher temperature to decompose it than ferrous sulphate, but is decomposed more readily than silver sulphate.

There is great difficulty in getting the whole of the copper sulphated. A greater amount is rendered soluble in the presence of much sulphide of iron.

Bankart's and Escalle's processes, both now abandoned, were based on this principle. In the former the copper was precipitated by iron, and in the latter as sulphide by calcium sulphide. This sulphide was subsequently reduced in a special form of furnace, and refined.

Much copper is extracted by calcining "low grade" pyritical ores in open heaps, washing out the sulphate formed in tanks, and precipitating the copper by iron.

Certain sulphide ores oxidise spontaneously on exposure to moist air. From this cause the water from copper mines, and drainage from cupreous waste heaps, often contain copper sulphate in solution. Extensive works were executed for precipitating mine waters in the Carnon Valley in Cornwall, at Pary's Mountain in Anglesea, and elsewhere. Both these methods are followed at the Rio Tinto mines.

Chloridising Processes.—The conversion of copper into chloride is effected by roasting sulphide ores with salt (sodium chloride), or by treating with some chlorinating agent, such as ferric chloride or manganese dioxide and salt, which, in the presence of sulphuric acid or sulphates, generate chlorine and hydrochloric acid.

Chloridising Roasting.—In roasting with salt, the sulphates produced react on the salt and form sulphate of soda.

$$CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4$$

Chlorine and hydrochloric acid are also generated in the furnace (see p. 276). The chlorine in the salt is ultimately transferred to the copper, which is converted into cupric and cuprous chlorides, the former soluble in water, and the latter in hydrochloric acid and chlorides.

Longmaid and Henderson's Processes.—This process is adopted for the treatment of the cinders from the burning of iron pyrites used in the manufacture of sulphuric acid. Portuguese, Spanish, and Norwegian pyrites, so largely imported for this purpose, contain from 1 to 2·5 per cent. of copper, which, after burning off the sulphur, reaches from 2 to 5 per cent. The "purple ore," as it is called, is ground down and mixed with a little small green ore (unburnt pyrites) and 10 to 18 per cent. rock salt in a mechanical mixer. This is roasted at a very low temperature, between 400° and 500° C. (copper chloride being volatile at a high temperature), for about 8 hours in a reverberatory or close muffle furnace (see p. 51). The roasted ore after withdrawal is lixiviated in wooden tanks, first with water and then with hydrochloric acid, obtained by passing the furnace gases up through condensing towers where the hydrochloric acid generated in roasting is dissolved out. The copper solution is run into settling tanks at a lower level, and then into precipitating tanks, where the copper is thrown down by iron. Generally, however, the ores treated contain gold and silver, and these are also extracted (see Claudet's Process for Silver). The "copper precipitate" is collected, fused, and refined.

In chlorination in heaps, the ore, part of which is calcined, is stacked in huge heaps mixed with salt, manganese dioxide, and residues from previous heaps. Open channels are left for the admission of air and moisture. Decomposition sets in with the production of ferric and manganese chlorides, which chlorinate the copper. The heaps are periodically drenched with water; or the heaps may be drenched with water containing ferrous chloride, etc., produced in the precipitation of the copper, to hasten the process. A series of

chemical reactions—somewhat involved—result in the conversion of the copper into chloride. The copper solution is precipitated by scrap iron.

Sulphuric Acid Leaching.—Treatment with sulphuric acid is now carried out on a large scale. The Ajo and Inspiration plants, Arizona, only date from 1917 and 1926 respectively. It was shown[1] that cuprous sulphide was soluble in acidified ferric-sulphate solution in addition to the solubility of the oxidised ores in the free acid. The reaction is as follows :—

$$Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$$

in two stages.

$$Cu_2S + Fe_2(SO_4)_3 = CuSO_4 + CuS + 2FeSO_4$$
$$CuS + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4 + S$$

If the solution containing the ferrous and copper sulphate be electrolysed with insoluble anodes the copper is deposited and the ferrous sulphate reconverted to ferric. The solvent is thus regenerated and is sent back to the treatment tanks.

$$CuSO_4 + 2FeSO_4 = Cu + Fe_2(SO_4)_3$$

The removal of the copper from sulphide ores is dependent on the ferric sulphate present. In starting the process it is necessary to ensure the presence of a sufficient amount by oxidation of added ferrous sulphate (Siemens-Halské process).

Copper cathodes are employed to receive the copper, but the anodes are of ferro silicon, fused magnetite, or carbon. Lead anodes, which are sometimes employed, are converted into lead peroxide and continue to serve when completely oxidised, but are liable to disintegrate. Lead anodes cannot be used with chloride solutions.

Treatment with Ferric and Cupric Chlorides.—Decomposition of sulphide ores also occurs when treated with ferric or cupric chlorides. Thus

$$Cu_2S + 2Fe_2Cl_6 = 2CuCl_2 + 4FeCl_2 + S$$

and

$$Cu_2S + \underset{\text{Cupric chloride}}{2CuCl_2} = \underset{\text{Cuprous chloride}}{2Cu_2Cl_2} + S$$

The cuprous chloride dissolves in the excess of iron and copper chloride in solution.

Oxides are also attacked and dissolved by ferric chloride. When the solution is electrolysed the cupric and ferric chloride are regenerated.

This is best done in depositing cells with a porous partition separating anodes and cathodes. Rich solution from the treatment tanks flows through the cathode—depositing—side, while poor solution from which the copper has been previously deposited flows through

[1] See Sullivan, U.S. Bureau Mines, Tech., 473, 1930.

the cells on the anode side. The chlorine liberated at the anode effects the regeneration of the solution.

It must be noted that solutions containing chlorides cannot be electrolysed with lead anodes. Where they are used chlorine must be eliminated.

At **Chuquicamata,** in Chili, the ore contains oxide, chloride, sulphate in large amounts $CuSO_43Cu\,(H_2O)_2$ and some cuprous sulphide and pyrite.

The crushed ore is treated by a sulphuric acid leaching method, spent electrolyte being used. This contains approximately 70 grms. of sulphuric acid per litre with 15 grms. copper, 4·5 grms. iron, 2·5 grms. nitric acid (from nitrates in ore), very small amounts of arsenic, antimony, or other heavy metals. Tellurium and selenium are absent, but a little free chlorine is present. After leaching the free chlorine is precipitated as cuprous chloride and the ferric sulphate[1] reduced to ferrous sulphate by the addition of copper precipitate in agitators. The cuprous chloride is settled out in tanks and the liquor electrolysed with insoluble "chilex" (copper silicide) and lead antimony grid anodes. Copper starting sheets are used as cathodes. Some 75 per cent. of the copper is deposited, and the remainder passes back into circulation with the spent electrolyte.

The cathodes are melted, refined, and cast into wire bar and cake. The cuprous chloride produced in removing chlorine from the solution is dissolved in brine or ferrous chloride solution, and the copper precipitated by scrap iron. Some of the precipitate is used as above, and the remainder melted and refined for market. The copper is very pure.

ANALYSIS OF CHUQUICAMATA COPPER.

Copper	99·9600
Oxygen	0·0320
Sulphur	0·0016
Arsenic	0·0002
Antimony	0·0004
Lead	0·0008
Tin	0·0006
Selenium, Tellurium, Bismuth, Manganese	0·0000
Iron	0·0016
Zinc	trace
Molybdenum	0·0001
Nickel	0·0000

Ammonia Lixiviation.—Cupric oxides and carbonates and some cupric compounds are very soluble in ammonia, giving a deep blue solution. This principle has been exploited for the treatment of some deposits of ore occurring in limestone and dolomite and tailings

[1] Ferric sulphate increases the electrical resistance in the cell.

containing these compounds. It is obvious that an acid leaching liquor could not be used owing to neutralisation by the mineral gangue. The crushed mineral is treated in large closed tanks 30 feet diameter and 15 feet to 20 feet deep with a false bottom. The charge is introduced through a central door in the top and discharged to conveyors through doors in the bottom.

The ammonia leaching liquor is stored in close tanks. Ammonia solution, partly saturated by treating a previous batch of ore, is first admitted from below and stands for 12 hours. (For satisfactory results the saturation of the ammonia by copper when withdrawn for recovery of the copper should not exceed 75 per cent.)

Part of this strong cupreous solution is withdrawn and sent for evaporation in stills. The ammonia is recovered and the copper precipitated as black oxide. Fresh ammonia and weak liquor is added to make up for that withdrawn, and the ore leached with this solution a second time, circulation being maintained for 36 to 48 hours.

When the liquor is withdrawn low-pressure steam is admitted above, to warm the ore and facilitate washing, giving practically a hot-water wash.

CHAPTER XIII

LEAD

Physical Properties.—The metal possesses a bluish-grey colour, and considerable lustre on fresh surfaces, which, however, are soon dimmed on exposure. It is soft enough to be impressed by the nail and to mark paper. Impurities, such as antimony, render it harder. It is malleable, ductile, and tough, but is very deficient in tenacity. Cast lead has only a tenacity of from 0·4 to 0·8 ton per square inch. After wire-drawing this is increased to 1 to 1·75 tons. Its melting-point is about 336° C., and it volatilises at very high temperatures. It contracts on solidifying, and is consequently unsuitable for castings. The specific gravity is 11·36, and is not increased by hammering. When alloyed with other base metals the specific gravity is diminished. It welds readily if the surfaces are fresh and clean, and even lead powder may be moulded by pressure into solid lumps. Alloys with tin may also be thus produced, and a compound sheet of the two metals may be formed by placing them in contact and passing through the rolls. The flowing power of the metal is great, and lead pipes and rods are squirted from a press. Lead crystallises on cooling from fusion. When heated near its melting-point, it breaks with a columnar fracture.

Chemical Properties.—Lead oxidises on exposure to moist air, forming suboxide of lead (Pb_2O). In a very finely divided state, as obtained by heating the tartrate, it takes fire and burns. When heated in air it readily combines with oxygen, and forms lead monoxide, **litharge** (PbO). This oxide is of a yellow colour; it fuses at a red heat, and yields, on cooling, a yellow crystalline mass. At a somewhat higher temperature it combines with silica, forming a readily fusible silicate of lead.

On this account it rapidly corrodes crucibles, retorts, and the sides of furnaces made with siliceous materials. Hence the necessity of employing bone ash or basic material in cupellation (p. 282), and the advantages of using water-jacketed furnaces in smelting operations. Mixtures of cuprous and lead oxides are even more corrosive than litharge alone. Litharge is largely used in glass making, and is made by oxidising lead on a cupel. See p. 283.

It exerts an oxidising influence on iron, nickel, zinc, and other metals, being reduced to lead. When heated with oxides of other metals, such as copper and iron oxides, litharge fuses and dissolves up the refractory oxide, forming a fusible mass. The amount of

litharge required varies. Thus 1 part of cuprous oxide requires 1·5 parts of litharge, while 1 of tin oxide requires at least 12.

If produced at a temperature below its fusion point, litharge has a brownish-yellow colour, and is known as *massicot*. If this be carefully heated in air it takes up more oxygen, and is converted into **red lead** or *minium* (Pb_3O_4).

Manufacture of Red Lead.—The metal is first "drossed,"[1] or oxidised in a low, reverberatory furnace, or "oven," with two narrow fireplaces, one on either side of the bed. The products of combustion escape through the working door in front, and are carried away by a hood surmounted by a chimney. The bed of the oven slopes slightly to the middle, and from back to front. In working, a dam of rough oxide, mixed with lead from the grinding of previous charges, is made across the front of the oven, some 20 to 30 cwts. of lead charged in and melted at a low red heat. The door is left partly open, and the oxide as it forms is pushed back, and the lead splashed about by a long iron paddle. The metal is continually thrown over the oxide at the back. Oxidation goes on freely, and the unoxidised lead drains to the front. Drossing is assisted by the addition of a little antimony to the lead. When the oxidation is completed, the charge is raked out into iron barrows and allowed to cool. It is then ground by millstones in a stream of water, which carries the fine material away in suspension. The unoxidised metallic lead and heavy particles of oxide are left behind in the troughs which lead to the settling tanks, where the finely divided massicot is deposited. It is collected and dried. It then constitutes "ground litharge." This is transferred to the "colouring oven," very similar to the drossing oven, except that the bed is flat. It is spread in low ridges over the bottom of the oven, and "coloured" at a lower temperature than that used in the drossing operation, being turned over from time to time. The red lead while hot has a deep brownish-purple colour, and is examined from time to time by the withdrawal of samples, and allowing to cool. When the oxidation is complete the cold sample has a bright red colour. It is again ground, levigated, and after drying and sieving, packed in barrels. Its composition is Pb_3O_4.[2] On heating it gives off oxygen and forms litharge, PbO. Treated with nitric acid, **lead peroxide**, PbO_2, is left as a purplish powder.

PbO_2 is also produced when lead or lead oxide forms the positive electrode in an electrolytic cell. Thus it forms on the plates of an accumulator during charging, the extra oxygen thus fixed being transferred to the other plate of spongy lead during discharge.

[1] In the latest methods this is preceded by a preliminary oxidation in a heated iron pot provided with a revolving paddle, steam and air being blown in. The lead is allowed to drip into the pot through an opening in the cover. The oxide is blown over into a depositing chamber and collected. The product is transferred to the drossing oven and produces a brilliant yellow oxide which is subsequently "coloured."

[2] It generally contains more lead than is required by this formula, and approximates to Pb_4O_5.

Red lead may be regarded as a compound of $2PbO,PbO_2$.

Action of Soft Water on Lead.—Waters containing oxygen in solution readily attack lead, but the action is retarded by the presence of carbonates and sulphates in the water. Lead pipes for conveying soft waters are coated inside with tin to prevent the water from being contaminated with lead.

Lead and Sulphur.—Lead combines readily with sulphur when heated, forming a brittle, grey, crystalline mass of lead sulphide (PbS). It has a high metallic lustre, and *melts at a higher temperature than the metal.* At a full red heat it is decomposed by iron, sulphide of iron and metallic lead resulting; thus—

$$2PbS + 2Fe = 2FeS + 2Pb$$

When calcined, lead sulphide is partly converted into oxide and partly into sulphate, SO_2 passing off.

The sulphate, which is also produced by the addition of sulphuric acid to a soluble salt of lead, is a white substance not readily decomposed by heat. It is insoluble in water. Heated with carbon, it is reduced to sulphide.

When sulphide of lead is heated with oxide or sulphate, the sulphur and oxygen combine and pass off as SO_2, metallic lead separating thus—

$$2PbO + PbS = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

Lead Ores.—The principal ores of lead are the sulphide, carbonate, and chlorophosphate.

Galena, *blue lead ore, lead sulphide* (PbS), is the most important and abundant. It is found both crystalline and massive. It has a grey metallic lustre, and is heavy, having a specific gravity of about 7·5. It is brittle, and contains 86·6 per cent. of lead. Galena occurs widely distributed in the older rocks. It is usually associated with quartz, fluor, calcite, barytes, and spathic iron ore in the veins, and frequently with copper pyrites and zinc ores. It often contains silver, sometimes in considerable quantity. Such ores are described as argentiferous. Iron, antimony, copper, and zinc are commonly present, and gold and bismuth also frequently occur in it. The localities are very numerous.

Cerussite, *lead carbonate,* or *white lead ore* ($PbCO_3$), also occurs. Its colour is white or yellowish, and its lustre adamantine to earthy. It has a specific gravity of 6·5, and contains 75 per cent. of lead. It is frequently argentiferous, like galena. The deposits at Leadville, in Colorado, and at Broken Hill, in Australia, are of this character.

Anglesite, *lead sulphate* ($PbSO_4$), also occurs, associated with galena and other lead ores.

Pyromorphite, *green lead ore, linnets, chlorophosphate of lead* ($3Pb_3(PO_4)_2,PbCl_2$), occurs in hexagonal crystals and as green and brown masses. Its specific gravity varies from 5·5 to 7·2. Ores in which the phosphorus is replaced by arsenic are known as *mimetesite.*

In addition to the above, many compounds of lead occur naturally, among which may be mentioned Boulangerite ($3PbS,Sb_2S_3$) and Jamesonite, another antimonial sulphide of lead.

Lead Smelting.

So many lead ores contain silver that the metallurgical treatment of the two metals is hardly separable. In this chapter we purpose dealing with the extraction and refining of lead, and such processes for the concentration of the silver as are conducted upon the lead, and to leave the actual recovery of the silver to be dealt with when treating of that metal. Extraction processes may be grouped, in much the same manner as in copper smelting, into reaction and reduction processes.

The *reaction* process for galena is based on similar chemical changes to those which occur in copper smelting, viz. the mutual reaction of the unaltered sulphide upon oxide and sulphate formed by roasting the sulphide. In the case of lead, however, the operation is simplified. The ore as received from the miner contains a sufficient percentage of metal to permit of its direct treatment.

$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + PbSO_4 = 2Pb + 2SO_2$$

The *reduction* processes may be divided into carbon reduction, where that element forms the reducing agent, and iron reduction processes, where iron, or iron-bearing materials, such as oxides of iron, or iron slags, form part of the charge, and liberate the lead from combination.

Reaction Processes.—To this category belong the Flintshire, Derbyshire, Spanish, French, and Bleiberg methods of smelting galena.

The form of furnace employed and the details of the process vary greatly, having regard to the purity of the galena or its admixture with carbonate, sulphate, etc.

The **Flintshire** furnace is shown in Fig. 121. It is a reverberatory furnace, having three doors opening on each side of the hearth. The bed—which consists of slag from previous operations, spread over the hearth while in a pasty state—is level with the doors on the labourers' side, but, on the working side, slopes so as to form a well some 18 inches deep, immediately in front of the middle door. A tap-hole C, communicating with the bottom of this, is provided for tapping out the lead. A second tap-hole above this, for the removal of fused slag, is provided in some furnaces. Outside the furnace is an iron pot, into which the metal is tapped. At the top of the furnace is a hopper, from which the ore is introduced into the furnace.

The process is conducted as follows. The charge of about a ton is let down from the hopper into the furnace, still red hot from a previous charge, and spread from the labourers' side over the furnace bed, clear of the well. It is then calcined at dull redness for from one

and a half to two hours, being stirred and turned over from time to time to expose it to the air, to admit which the doors are left partly open. During this stage the fire is kept low and the temperature is not sufficient to melt the galena, which, it may be noted, has a higher melting-point than lead itself. During this stage oxidation occurs freely, oxide and sulphate of lead being formed.

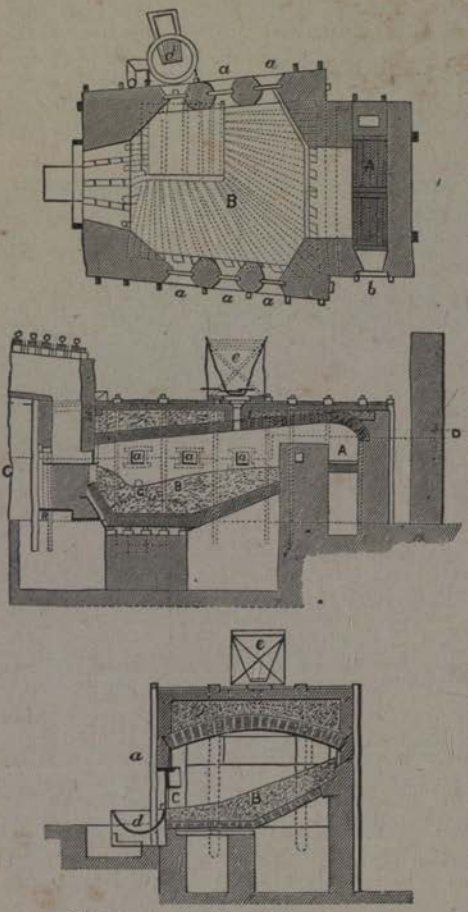


FIG. 121.—Lead smelting furnace.

The doors are now closed, the fire made up, and the temperature raised to full redness, when the reaction between the oxide, sulphide, and sulphate produces a copious separation of lead, which collects in the well of the furnace. The temperature at this point is also somewhat below the melting-point of galena. The separated lead is tapped from the furnace.

The unreduced mass becomes soft and pasty. It is pushed out of the basin and spread over the hearth. To prevent its fusion, the doors are opened to cool it somewhat, and it is stiffened—"set up"—by the addition of a little lime and again calcined, being well turned over for about half an hour.

The charge is then melted—"flowed"—down by increasing the temperature, for which purpose the doors are closed, the damper opened, and a fresh fire made. The lime decomposes any silicate of lead formed, liberating lead oxide. This and the oxide produced by calcining react on the unaltered sulphide present, and a further separation of lead occurs. Lime is again thrown in and mixed with the slags to render them pasty, and they are again spread over the hearth and roasted for from half to one hour. At the end of this period the fire is again made up, the temperature is raised to its highest

point, and the whole is melted a second time. The oxide produced during the roasting and that liberated from silicate by the lime added is in this stage often more than sufficient to decompose the remaining sulphide, and a little coal slack is often added to assist in its reduction. This also reduces any sulphate to sulphide, which reacts on the oxide, producing lead. The metal is then tapped into the lead-pot in front.

The slags are "dried" by further additions of lime, and are withdrawn in a pasty state from the furnace. They are known as grey slags, and usually amount to about 20 per cent. of the charge. They contain about 40 per cent. of lead as silicate and sulphide, which is recovered in slag hearths.

In modern practice where reverberatory furnaces are employed the latter part of the operation is modified. After the second roasting and fusion the residual slags are raked from the furnace and smelted in the blast furnace. In this case the recovery of lead is about 80 per cent. as compared with 90 per cent. The treatment in the blast furnace is more economical.

Setting up by lime has a twofold object. Its principal use is to stiffen the slags and render them infusible during the roasting periods, so that the galena contained in the charge shall not become bound up, and protected from the action of the air. In the fusions it probably liberates oxide of lead from the silicate.

The metal in the lead-pot is covered with slags, matte, and dross, which retains much metallic lead in globules. Coal slack is thrown on and stirred into the hot metal. The gas produced burns on the top, heats the slag, and releases the shots of metal. The skimmings are either thrown back into the furnace at once, to further separate lead, or are added to the succeeding charge during the preliminary calcining. The lead produced is tapped out about an hour from the commencement of the process.

The stages of the process are known as "fires."

When barytes occurs as gangue in the ore, it is necessary to add fluorspar as a flux, or to mix it with ore containing fluor. The amount of blende and other sulphides in the ore also influences the fusibility of the slags.

The processes in use at Cuëron, Bleiberg, and elsewhere are of a similar character. This process is only applicable to **pure** ores. Foreign sulphides such as antimonite and even copper pyrites combine with galena, and form readily fusible double sulphides, which melt or clot, and arrest the roasting.

In smelting lead ores containing antimony in reverberatory furnaces by the reaction process, the lead obtained in the earlier stages is freer from that element than that subsequently produced.

Smelting in water-jacketed blast furnaces has almost superseded other methods of smelting.

Reduction Processes.—These are conducted in both reverberatory and blast furnaces. They are employed for the treatment of impure ores and slags, and for reducing the oxides, dross, or *abstriches* produced in the purification of lead.

In the treatment of raw ores, iron is the reducing agent generally employed. With poor ores containing much iron sulphide, a preliminary roasting and fusion were resorted to, for the purpose of fluxing off the iron and concentrating the lead.

The Cornish Process.—This process is followed to some extent for the treatment of impure ores containing copper and antimony, reguli containing lead, and also for the treatment of slags.

The ore or regulus is first roasted in a separate calciner, much as in copper smelting, for from 15 to 18 hours.

It is then smelted in a furnace resembling a Flintshire furnace. The charge of 2 tons is melted down in from 2 to 3 hours.

With impure ores, or with substances rich in silver, the lead which separates by "reaction" is removed and dealt with separately. In the former case it is purer, and in the latter richer in silver than that subsequently produced.

Lime and anthracite culm are then added and well mixed. The materials, thus rendered stiff, are spread over the hearth, and some 2 cwts. of scrap iron added. The doors are closed and luted, and the charge remelted at a high temperature. The products separate in layers, which follow each other when the furnace is tapped: *Lead*, which is received in the lead-pot in front; *regulus*, or slurry, which is a mixture of iron sulphide, with the copper and some lead sulphide which flows over the top of the lead-pot into the pot below; and *slag*, which is generally so free from lead and copper as to be thrown away.

This process occupies about 8 hours.

In this process the lead first obtained is the result of reaction between oxide, sulphide, and sulphate; in the second stage the sulphide and silicate present are reduced by the iron. The anthracite reduces the oxidised matters present.

$$2PbO,SiO_2 + 2Fe = 2FeO,SiO_2 + 2Pb$$

Lead Smelting in Blast Furnaces.—*Modern lead smelting* is carried out mainly in blast furnaces of the waterjacketed type. These differ from those used in copper smelting. Owing to the lower temperature employed it is only necessary to water cool the lower section of the furnace carrying the tuyères. A large amount of fume is produced, and it is necessary to close the furnace throat and provide dust and fume catchers. In the diagram (Fig. 122) the charging pipe is kept full and the gases withdrawn through N. More often enclosed tops with charging doors or bells through which the ore cars drop the charge are provided.

Many furnaces are constructed with a "metal" sump and syphon tap—a modification of Richardson's furnace (Fig. 123).

The lead flows as reduced from the bottom of the sump and is free from scoriæ or slag. The lower melting-point of the metal enables this to be done.

As in all blast furnace smelting practice it is necessary to maintain a clear way through the charge and prevent packing to avoid "hanging" of the charge.

Since lead ores are usually highly dressed and largely in a fine state of division—especially flotation products—preliminary treatment is necessary to bring them to a satisfactory condition for blast furnace smelting. This takes the form of calcination and agglutination by heat, which is carried out in various ways.

The lead in the charge is thus generally in the oxidised state, and the reduction is mainly effected by the carbon in the fuel. Sulphide ore is calcined often to less than 1 per cent. sulphur.

If sulphide or sulphate remains in the charge its reduction is effected (*a*) by iron; (*b*) by reaction; or (*c*) by the joint action of iron and carbon, iron reduced from the iron oxide in the charge probably being the active agent.

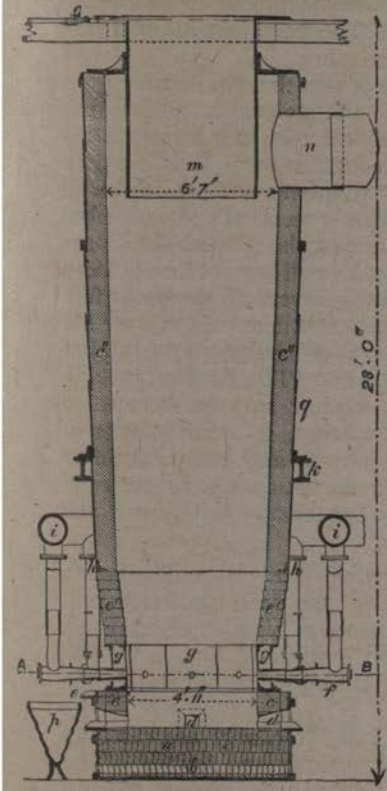


FIG. 122.—*a*, hearth bottom; *b*, channels in brickwork; *dd*, tap holes; *e*, slag lip; *f*, blast pipes; *g*, water-jacket; *i*, blast main; *k*, supporting ring; *m*, charging pipe; *n*, waste gas pipe; *o*, charging floor; *p*, slag pot.

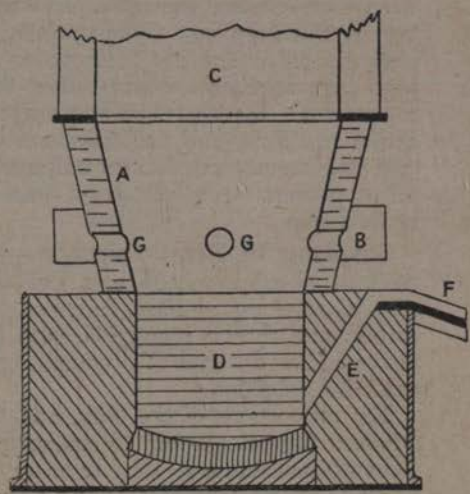


FIG. 123.—Lower part lead furnace, showing syphon tap. A, water-jacket; B, air belt; C, furnace shaft; D, metal sump; E, syphon tap; F, metal spout; G, tuyères.

Calcination and Sintering are carried out in various ways.

Long multiple bedded reverberatory furnaces with a "fuse" box at the discharge end are sometimes used. They have the beds at only 3 inches difference in level. The end bed is hot enough to soften the charge and clot it up, not actually melt it. It is raked out.

The Dwight-Lloyd roaster is an endless steel link belt carried on rollers which travels slowly.[1] At the top, the belt passes over a suction box with which it forms a seal. The ore is dropped on the belt at one end, levelled and passed under a fire-box or burner. It is thus ignited, the fire gases and air being drawn downwards through the layer of ore. As it is carried slowly along beyond the fire-box the sulphur in the ore continues to burn. It may complete the calcination or prepare the ore for " pot " roasting. The material falls off at the further end of the belt as it turns over the roller.

Pot roasting is carried out in deep iron pots with an air blast.

In the Huntingdon-Heberlin process the galena is mixed with 10–15 per cent. of lime and first partially calcined in a reverberatory furnace, the final calcination being effected in the pot. This is a deep more or less conical vessel, mounted on trunnions, and provided with a hood to carry away the sulphur dioxide generated. An air blast is admitted at the bottom under a perforated plate, which distributes it uniformly to the charge. Red-hot ore or a small layer of fire is placed on this and the partially roasted ore added in layers till the pot is full. After each addition the action is allowed to continue till the layer has become fairly ignited. When full the blast is continued till the sulphur is eliminated. The pot holds 10 to 11 tons. The reactions taking place are somewhat obscure, but the sulphur may be reduced to 1 per cent. In other similar processes calcium sulphate (plaster of Paris) and limestone and silica are employed, and the preliminary calcining is omitted, but the sulphur should not exceed 18 per cent. Silica present forms silicate of lead. The charge is dumped and broken up.

Smelting in Blast Furnace.—Carried out on oxidised and calcined (desulphurised) ores containing the lead as oxide and silicate, smelting in blast furnaces becomes a simple reduction by carbon and carbon monoxide, with iron oxide and lime acting as fluxes and as a means of decomposing the lead silicate liberating the oxide for reduction.

The proportions of ore, flux, and fuel in the charge are carefully adjusted (by calculation) to ensure free working and fluidity of the slags without undue heating in order to minimise the amount of fume which is always considerable and a source of difficulty.

Fresh additions are made to the furnace at regular intervals as the charge melts.

Attention is paid to the flow of slag and lead and the condition of the tuyères and the flow of water through the water jackets to ensure regular working.

Sulphur.—When sulphur is present in the charge in sufficient quantity it may combine with iron and copper and produce a matte. This carries the whole of the copper, some gold—if present—lead, and other metals as sulphides. In some cases this method is used when treating cuprous ores containing precious metals as at

[1] See Appendix.

Freiberg. The fused products separate in three layers, lead, matte, and slag.

The lead carries the silver, most of the gold, as well as antimony, tin, bismuth, copper, and traces of nickel, cobalt, and arsenic. It is generally more impure than that produced by reaction processes. The matte consists essentially of sulphides, iron, and lead, and nearly the whole of the copper in the charge.

It sometimes contains 10 to 12 per cent. of lead and some silver, gold, etc. It is calcined and resmelted in a separate furnace, when it yields lead (often rich in silver), a second matte richer in copper, and slag. The second matte is again calcined and smelted, yielding a regulus which may contain over 20 per cent. of copper and slag. This matte is treated for copper. Sufficient sulphur is left in the mattes after calcining to serve as a vehicle for concentrating the copper. The oxide of iron formed during roasting is fluxed off by the addition of silica in the fusion (see Copper). Slags from the smelting of *first* matte generally contain lead, and are resmelted. Lead obtained from matte is very impure.

If arsenic be present some speiss may be produced, see p. 45.

Slag.—The slag from blast furnace smelting is a well-fused slag, generally more or less glassy in character. It is run continuously from the slag spout into bogies, usually through a catch-pot.

It seldoms conforms to any chemical formula, but is essentially a double silicate of lime and ferrous oxide with more or less alumina and other metallic oxides approximating to a mono-silicate. The gangue of the ore varies in different localities, being in some cases siliceous and in others limestone or dolomite. Fluxes are added to produce the smallest amount of clean free-running slag, siliceous matters, limestone, and oxide of iron or materials containing it as may be necessary. Alumina, and especially zinc oxide, have a tendency to stiffen slags. Together they tend to produce zinc spinel. In the latter case it is made more fluid by increasing the proportion of iron oxide.

The lime (including magnesia), ferrous oxide, and silica usually total 90 per cent. of the whole, the remaining 10 per cent. being made up of alumina, zinc, and other oxides. The largest amount of zinc oxide that can be readily carried with fluidity is about 22 per cent. at the temperature of smelting. If the proportion of oxide of iron in the charge is excessive there is a tendency to produce magnetic oxide of iron which does not combine with silica. It is difficultly fusible and renders the slags pasty.

Lead furnace slags contain—

Silica	28–37 per cent.
Lime (including magnesia) . . .	16–21 „
Ferrous oxide	30–45 „

If more than 1 per cent. of lead is present it is re-melted.

With ores containing baryta, sulphate of barium—a common impurity in some ores—difficulty may arise. It can be fluxed by fluor-spar, also a common occurrence. At high temperatures it may be reduced to sulphide and act as a sulphurising agent. See Nickel p. 328.

It must be remembered that in smelting processes the precious metals have always a tendency to associate themselves with the metallic products of the operation. In the few cases where two such products are obtained—lead and matte—the lead carries the greater part, but the matte also contains some, notably gold. In the subsequent treatment of the matte much of the silver and gold contained pass into the lead produced. That carried away finally by the matte passes into the copper and is recovered in electrolytic refining.

The slag hearth (Fig. 124) is a small blast furnace formerly used for treating the rich grey slags obtained in smelting in reverberatory furnaces.

Rectangular in form, about 26 inches by 22 inches internal dimensions, the hearth itself is 3 feet deep. The back below the tuyère is iron

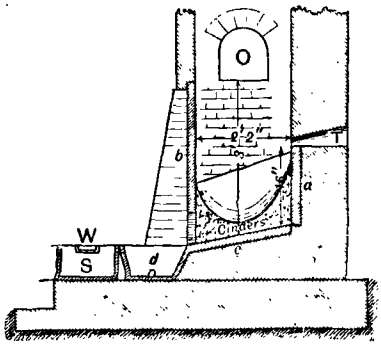


FIG. 124.—Slag hearth.

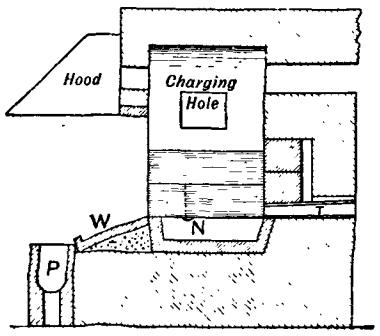


FIG. 125.

plates (*a*). The front also is an iron plate (*b*), supported some 7 inches above the bed plate (*c*), which slopes toward the front to permit the separated lead and slag to flow towards the exit. The distinguishing feature of this hearth is the bottom, shaped as shown, made of cinders. Metallic lead does not "wet" the cinders, and as it is reduced it filters like mercury through the ash bottom and runs out into the lead pot in front, also filled with cinders. The slag does "wet" the ash, consequently does not pass, and is retained in the furnace. It is removed by tapping through a hole made in the clay stopping of the front. It flows over the top of the ashes in the lead pot into the pot beyond. All the reactions are similar to those already dealt with. It can only be worked intermittently, as it gets too hot. Circular cupolas and water-jacketed furnaces are now used for slag reduction and in a few cases reverberatory furnaces.

Combined Reaction and Reduction Processes.—The ore hearth shown in Fig. 125 was formerly in use in Scotland and the North of England.

The hearth consisted of a rectangular cast-iron trough N, the sump 3 inches thick, 22 inches square, and 4½ to 6½ inches deep, bedded in sand on a raised platform as shown, with sides and back made of cast-iron prisms 6 to 8 inches thick,

giving a hearth 16 to 18 inches deep, open in front, surmounted by a brickwork hood. In front of the hearth was an inclined iron plate 3 feet by 1½ feet—the workstone—on which the partially fused mass was withdrawn and sorted to release reduced entangled lead which ran down into the lead pot P and reject slag. A diagonal groove in the workstone directs the lead to the pot. Any unsmelted material was returned to the hearth.

A single tuyère entering at the back provided air for burning the peat or coal employed, and the whole charge floated on the top of the lead bath with which the sump became filled. When full the lead, as it was reduced, drained down a diagonal groove in the workstone to the lead pot. The hearth was charged from the side opening shown and kept practically full.

Both raw and calcined galena and other ores were treated. The reduction takes place partly by reaction, oxides and sulphates being produced in the preliminary roasting or by the excess air supplied by the blast, and partly by direct reduction by carbon. Lime was added as necessary to stiffen the charge and prevent its fusion. The slag more or less similar to that from reverberatory smelting had to be smelted in slag hearths.

The low temperature prevailing throughout favoured the production of lead of good quality, the impurities not being reduced.

A hearth yields about 70 cwts. of lead in 24 hours, and consumes about 12 cwts. of coal.

The loss as fume varies from 7 to 20 per cent. of the lead.

Softening or Improvement of Hard Lead.—The pig lead, as obtained from many operations, contains various impurities, antimony, tin, copper, zinc, sulphur, iron, silver, and bismuth being often present. Their effect is to harden the lead and unfit it for the purposes to which it is generally applied. The foreign metals are removed by oxidation, the lead being exposed at a red heat to the action of the air in a reverberatory furnace, the bed of which sometimes consists of a cast-iron pan—some modern furnaces are capable of holding 200 tons—or one of wrought iron, with a fire-brick lining, or is made of slags. In the latter cases higher temperatures can be employed, and the process occupies less time. The lead is ladled or run in from a melting-pot, or the pig lead may be melted in the furnace.

The oxides which form, consisting of oxide of lead mixed with those of the impurities, are skimmed off from time to time to expose fresh surfaces, lime being added, if fused, to stiffen them. Samples of the metal are withdrawn and cast. When the lead shows a peculiar flaky appearance the operation is judged complete, and the lead is ladled out or run into iron pig moulds.

When much copper is present the lead is *liquated* before softening, as that element is not removed to any great extent. This is accomplished at Clausthal on the bed of a reverberatory furnace, which slopes slightly upwards from the fire-place. The temperature of the flue-end of the hearth is below the melting-point of lead. The metal is introduced there, and gradually moved forward. The lead melts and drains away, and the residues are moved gradually nearer the fire to sweat out all the lead, and are then raked out of the furnace. This residue contains the copper and nickel and cobalt, and often some arsenic and sulphur.

Softening Blast Furnace Leads.—The lead produced by modern smelting methods is much less pure than that obtained by

reaction. The drosses during improvement may amount to 25 per cent. of the lead.

In large plants the primary drossing is carried out in huge kettles. These may have a capacity of 235 tons and are made of 1-inch welded steel, provided with special appliances for skimming and handling the dross. The scoop used for this purpose has a capacity of 1000 lbs. and is operated by a crane, the skimmings being transferred directly to a strongly heated reverberatory furnace for treatment. This furnace has a water-cooled mechanically operated door in the arch for purposes of charging. Mechanically held lead is separated and run back to the drossing kettle.

In some cases, where much copper is present, the drossed metal is treated with sulphur—Hulst process—and the dross, containing the copper as sulphide, added to the other drosses in the furnace.

The drosses melt forming a matte (matte speiss). This is run out and sent to the copper plant.

The drossed metal is transferred to a 200-ton reverberatory furnace for softening in the ordinary way before desilverising.[1]

The Betterton Process.—Bismuth is removed from lead by the addition of metallic calcium and magnesium with which it alloys, and is brought to the surface and oxidised. The amount to be added depends on the quantity of bismuth present and the agitation.

With low bismuth contents it has been found more economical than the Betts electro-refining process, and in some cases, as at Grasselli and other American centres, the Betts[2] plant has been closed down.

Reduction of Litharge and Drosses.—The "drosses," or "abstriches"—impure litharge—formed during softening or other operations, may be reduced by intimately mixing them with small coal, grinding them together under edge-runners, and smelting in a reverberatory furnace, the bed of which is protected from corrosion by a layer of coke; this is formed by introducing a few inches of moistened caking-coal slack into the furnace, and beating it down. The bed slopes slightly, and the reduced lead drains into a basin in front.

Small water-jacketed furnaces are now largely employed for this purpose. The hard lead obtained, marked H, is richer in antimony, etc., and is again softened. The dross yields on reduction hard hard —HH—lead, and so on. The process is repeated, until lead rich in antimony—sometimes more than 50 per cent.—is obtained. This is sold to the type-founders (see Alloys, p. 343).

Desilverisation of Lead.—Silver, as before noted, is commonly found in lead ores, and during smelting passes into the metal. Lead containing more than 9 ounces of silver to the ton is treated for its extraction. Two methods are followed for this purpose.

Pattinsonising.—In Pattinson's process, advantage is taken of the fact that alloys of lead with silver containing less than 2·25 per cent.[3] of silver, have a lower melting-point than pure lead, and that

[1] Litharge may be added to accelerate the oxidation of arsenic, tin and antimony in the order named but with much overlapping.

[2] See p. 257.

[3] 735 ozs. per ton.

lead in the solid state is denser than when molten. In consequence of this, if a large body of lead be melted and cooled slowly with constant stirring, the lead which first crystallises is poorer in silver than that which remains fluid. By removing the crystals with perforated ladles, a fluid alloy richer in silver and a lead poorer than the original are obtained. The crystals removed are, of course, covered with the fluid alloy, and thus, in the process of removal, some silver is also carried off. By repeating the process on the enriched alloy

FIG. 126.

the silver contents of the fluid portion are again increased, until an alloy containing sufficient silver to be cupelled is obtained.[1]

Or, the rich alloy may be treated by the Parkes process, which see.

The process is conducted in a series of iron pans set side by side, as shown in Fig. 126, each capable of holding from 10 to 15 tons of lead. A 15-ton boiler is 5 feet 2 inches in diameter, and has a capacity of 43 cubic feet. A full set of pots numbers 13. Each pot is heated by its own fire, which is controlled by a damper. The products of combustion pass from the fireplace into a flue encircling the pot, and thence to the main flue.

The crystals are removed by a perforated ladle made of half-inch plate, 16 to 20 inches in diameter, 4 to 6 inches deep, with a handle about 9 feet long, about half the length being iron and the other wood.

[1] In practice it is not possible to concentrate beyond 1·8 per cent. silver = 588 ozs. per ton.

A chisel-ended iron bar is used to break up the lead crusts and for stirring, and a flat, perforated shovel for skimming.

Small pots filled with melted lead, between each pair of boilers, are sometimes provided for keeping the ladles hot, and the range of boilers is commanded by a crane for the transference of the ladlesful of crystals removed, or pivoted rests some 18 inches high with a roller top are placed between the pots. These are used as fulcrums for resting the handle of the ladle while fishing out the crystals and "turning over" from one pot to the next.

The lead to be desilverised is first melted in one of the pots, and got sufficiently hot to oxidise. A scum of dross forms and is removed. (If very impure, it is necessary to liquate and soften before Pattinsonising.) The fires are then withdrawn, and the cooling down facilitated by sprinkling water on the surface. The crusts of lead which form are pushed down into the metal, until there is difficulty in melting them; the water is then stopped and the bath thoroughly paddled. As the mass further cools, the lead begins to solidify in crystals. These are larger as the alloy is poorer in silver. Being heavier than the molten alloy, they sink, and the lead requires to be continually stirred and broken up, to prevent the formation of masses of crystals, which would entangle rich lead. The temperature must be carefully managed, or the crystallisation will either be too slow, or masses of crystals will form. When the formation of crystals has progressed sufficiently they are removed by the ladles and transferred to the next pot to the left, which is already hot enough to melt them. Each ladleful as it is raised to the surface is allowed to drain, and shaken to remove the liquid as much as possible. In this manner two-thirds or seven-eighths of the lead is removed. The former method is known as the "high" and the latter as the "low" system.

Working on the high system all the lead removed is thrown into the next pot. In the "low" system of working the last eighth contains too much silver, and is thrown on the ground, to be used with lead of the same richness in silver. The fluid alloy remaining in the pot is transferred to the next pot to the right. Working on the high system, it contains about twice the proportion of silver in the original lead, while the poor lead passing to the left averages about one-half.

By repeating the process on the enriched lead the proportion is again doubled, while the poor lead, similarly treated, will be again halved. Starting with a 10-oz. lead, one-third rich lead, assaying 20 ozs., and two-thirds poor lead assaying 5 ozs. to the ton will be obtained. On again treating the enriched alloy, 40 ozs. rich and 10 ozs. poor will be obtained. A third treatment yields 80 ozs. rich and 20 ozs. poor; a fourth, 160 rich and 40 ozs. poor; a fifth, 320 ozs. rich and 80 ozs. poor, and so on.

The *poor* lead, from the first crystallisation, on a second treatment, yields 10 ozs. rich and $2\frac{1}{2}$ poor; a third treatment gives 5 ozs. rich and $1\frac{1}{4}$ poor; and a fourth treatment gives $2\frac{1}{2}$ ozs. rich and $\frac{5}{8}$ poor; These figures are only a general statement; in practice they are not always realised.

In actual work, alternate pots are generally being crystallised at the same time, so that the rich third from the one and the poor two-thirds from the other, make up a charge for the intervening pot.

When less than 1 oz. of silver per ton is present the poor crystals are transferred to the market pot on the extreme left, which has a capacity of only about two-thirds of the others, and from which the lead is cast into pigs.

The *rich* lead, containing from 500 to 600 ozs. per ton, is cupelled (see p. 251).

The Pattinson process is now mainly followed for the enrichment of leads too poor to be treated by zinc, as described (see Parkes' Process).

The oxidation of the lead which accompanies the repeated meltings so purifies it that, by the time it reaches the market pot, there is no need for further softening, and it is cast into pigs.

Note.—The copper, antimony, bismuth, and nickel remain mostly in the fluid portion, and would give trouble—especially antimony—in the cupellation of the enriched lead. Before Pattinsonising, it is "improved" if more than 0·5 per cent. impurity is present.

Rozan Process.—Pattinsonising by steam.—This method was introduced by Messrs. Luce and Rozan at Marseilles, and has been adopted to some extent. The difference consists in the method of stirring up the molten lead by means of steam at high pressure forced through the lead, the surface being cooled by water as before. The crystals are not removed, but the liquid-enriched alloy is run off from the bottom of the pot and the crystals remain behind. Lead of the same richness as the crystals is run in from a melting-pot above, and the operation repeated. A great saving in labour, fuel, and drosses results. (Fig. 127.)

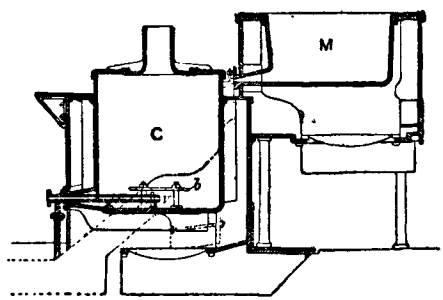


FIG. 127.—Melting Pot M and Treatment Kettle C for Rozan Process.

Parkes' Process.—Desilverising by zinc.—This process has displaced, to a very large extent, the Pattinson method of desilverising. Or the "work lead" is Pattinsonised until it has attained a richness of about 40 to 60 ozs., and is then treated with zinc.

The process depends on two facts. *First*, that zinc and lead melted together do not alloy, but separate according to their specific gravities, the zinc rising to the surface, carrying only some 2 per cent. of lead.

Second.—Silver (as well as copper and antimony, which behave in a similar manner) alloys with zinc more readily than with lead, and

hence, when that metal is mixed with argentiferous lead, the silver is collected in the zinc scum which rises to the top and is removed.

The method of carrying out the process varies somewhat in different works, and the quantity of zinc required depends on the amount of silver present.

The arrangement of the zincing portion of a Parkes plant is shown in plan in Fig. 128. The two large pots, A, are capable of holding 25 to 60 tons of lead, and are employed in the addition of the zinc. The smaller ones, B, have a capacity of about 6 tons, and are for the treatment of the zinc crusts on removal. D is a reverberatory furnace for removing the zinc taken up by the lead, by oxidation.

The lead is melted in one of the pots A, heated to the melting-point of zinc, and skimmed. A portion of the zinc is then added, and when this has melted a further addition of zinc is made, and the whole is well paddled for some 15 minutes. The pot is then covered over and allowed to rest for a period, varying from 1 to 3 hours.

While at rest the zinc gradually rises to the top, carrying with it the silver. As it cools it forms a crust on top, in which a good deal of lead is entangled. The zinc crust is removed by a ladle into the middle of the smaller pots, and skimming continued till the lead begins to set. The pot is again heated up, and a second addition of zinc made to the lead, well paddled in, and again allowed to cool. The amount added depends on the amount of silver remaining in the lead. The crusts formed are removed as before. After this second treatment the lead is desilverised and is then run or syphoned off into the improving furnace D, to remove the zinc retained by the lead. This amounts to about ½ per cent. The lead is skimmed from time to time. Samples taken out are cast in moulds and examined. When the surface indicates a sufficient degree of purity, the lead is run from the furnace into a lead-pot, E, allowed to cool down, and cast.

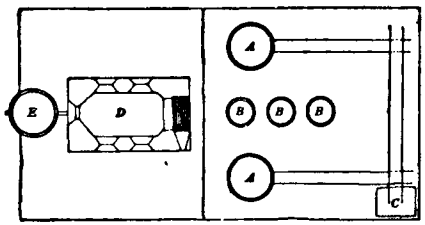


FIG. 128.

Note.—With lead containing more than 80 ozs. of silver, the addition of the zinc in three portions is advisable.

The first crusts removed to the smaller pots are gently heated to liquate out adherent lead. This is either cupelled, or generally returned to the zincing-pot with the next charge. After liquation, the crusts are transferred into the right-hand pot, and sent off to be distilled. They contain about 80 per cent. of lead. The last crusts are used as the first addition of zinc made to the next charge.

The total amount of zinc required varies. A 20-oz. lead requires

30 lbs. of zinc per ton, equal to 1·33 per cent.; a 40-oz. lead requires 35 lbs., equal to 1·56 per cent.; and a 60-oz. lead about 38 lbs., equal to 1·69 per cent.; while a 500-oz. lead requires about 2½ per cent.

In **Cordurie's** process, the zinc to be added is enclosed in a perforated cast-iron box, fixed on the end of a revolving vertical shaft. Immediately above the box is a propeller-shaped paddle, which as the zinc melts distributes it uniformly through the lead and thoroughly mixes it. Three additions of zinc are made.

The softening is effected by running the lead into a pot situated at a lower level, heating it to redness, and blowing superheated steam through it succeeded by a mixture of steam and air. The zinc and iron present decompose the steam and are oxidised, hydrogen being liberated. Later, the copper and antimony remaining are oxidised by the air.

Williams' Process.—The new continuous desilverising process of G. K. Williams, just completed at Broken Hill Associated Smelters, is a modified application of Parkes' process. A tall pot or kettle is employed. The temperature is highest at the top and is capable of keeping the zinc-rich alloy molten.

By establishing a continuous temperature gradient in the molten lead occupying the lower part of a vertical kettle the separating silver-rich zinc alloy rises to the top of the lead. The upper part of the kettle is occupied by a liquid zinc-rich silver-zinc alloy which dissolves and absorbs the silver-rich rising from the lead. The removal of the zinc by skimming and the liquation of the skimmings is thereby avoided. Silver-free lead is withdrawn from the bottom of the kettle.

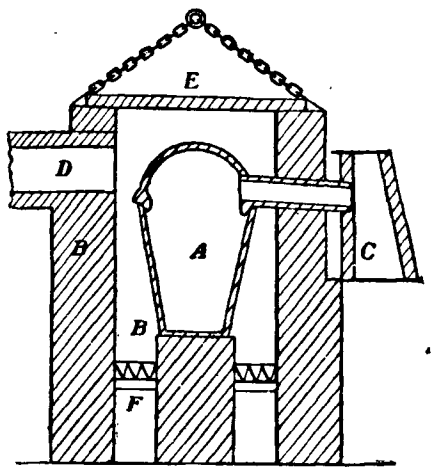


FIG. 129.—Furnace for distilling zinc crusts.

A similar process for the removal of arsenic and antimony prior to desilverising and the removal of zinc afterwards has also been developed.

Treatment with **chlorine** for the removal of zinc after desilverising has become common. The zinc being preferentially attacked, the gas is bubbled through the molten lead, zinc chloride being formed.

Treatment of Zinc Crusts.—The zinc crusts carry in addition to the silver a large proportion of lead, together with the copper, and some antimony, arsenic, and nickel.

The zinc is distilled off in large plumbago crucibles, A, standing on a pillar in a furnace, B, as shown in Fig. 129. The pots are about 18 inches in diameter and 27 to 30 inches high, provided with a cover which is luted on. A clay pipe leads from a hole in the side of the

cover to the condenser, C, standing in front, in which the recovered zinc condenses. D is the flue, E the cover of the furnace, and F the firebars. A little lime and coal-dust are often added. The residual lead is cast in moulds, and afterwards cupelled. Any bismuth, antimony, copper, etc., in the crusts remain with the lead, which may contain 2,000–4,000 ozs. of silver per ton.

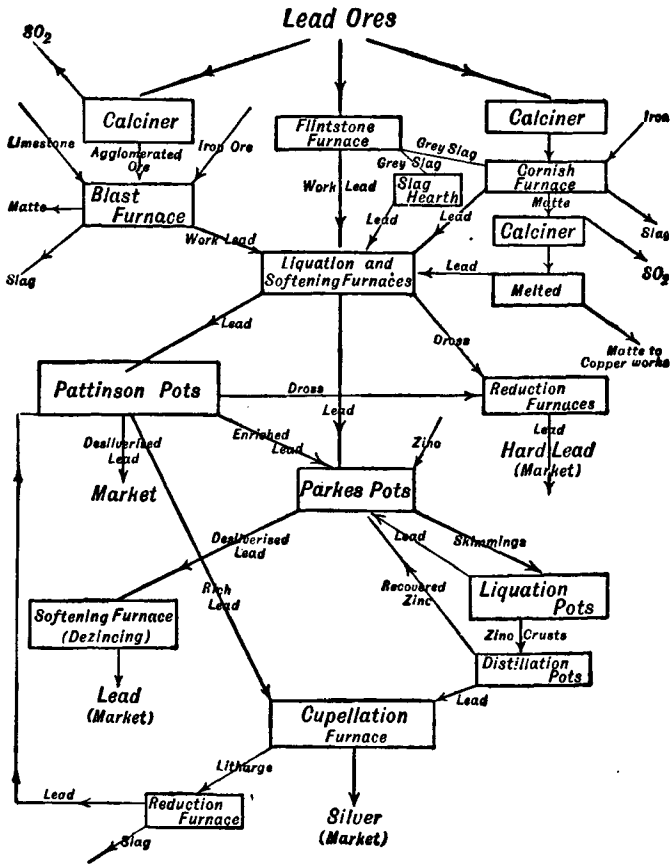


FIG. 130.—Synopsis of lead smelting and desilverising processes.

Tilting retort furnaces are also largely used. They have bottle shaped retorts.

Lead Fume.—The gases passing away from the various furnaces carry with them considerable quantities of dust and volatile compounds of lead. These are deposited in the flues through which the gases are conveyed to the chimney-stack, and constitute "lead fume." It consists principally of lead sulphate, with some oxide and sulphide,

and also lime, oxide of iron, alumina, etc., carried over as fine dust, and some silver. Zinc oxide is often present, especially in blast-furnace flues. A crust of this substance is often found in the upper part of the furnace when smelting zinciferous ores in blast furnaces.

For the condensation of the fume, and to minimise the nuisance arising from noxious vapours, the flues with which all the furnaces are connected were sometimes 3 miles long, and measured as much as 8 feet by 9.

Staggs, Stokoe, and French and Wilson have introduced condensers in which the gases are washed, or caused to pass through a wet filter of faggots, gauze, or sawdust, etc., and thus deposit the solid matter.

Bag filters in which the gases after cooling are drawn by suction through long canvas or flannel bags are largely employed.

The Cottrell process for securing the deposit of the fume by silent discharge of electricity at high potential—70,000 to 100,000 volts—has been adopted.

The fume is smelted in blast furnaces, being previously agglomerated by heat to facilitate charging.

Electro-refining of Lead.—Betts' process for electro-refining is specially applicable to lead containing bismuth. At Omaha the metal contained 1·5 per cent. bismuth.[1] The electrolyte is silico fluoride of lead ($PbSiF_6$) in hydrofluosilicic acid (H_2SiF_6), 5–10 per cent. lead and 8–12 per cent. H_2SiF_6. Small additions of gelatine are made. The crude lead, cast into anodes 375–400 lbs., has a purity of 97–98 per cent. The tanks are arranged as in copper refining. Zinc, nickel, cobalt, and a little antimony pass into solution, but bismuth, antimony, arsenic, selenium, and tellurium, together with the silver and gold, remain in the mud. Tin, if present, dissolves and is deposited with the lead. A current density of 1·5–1·7 amps. per square decimetre with a voltage of 0.3–0·35 volts per tank, at a temperature of 25–40° C., is employed.

[1] This metal is not removed in desilverising.

CHAPTER XIV

MERCURY

THIS is the only metal which is fluid at ordinary temperatures. About $-39°$ C. it freezes to a leaden grey, hard, malleable mass, contracting considerably on solidifying.

Its silvery white colour, and the readiness with which it moves about, owing to not wetting the surfaces (except metallic) with which it comes in contact, has earned for it the name of quicksilver (German "quick silber"). Its specific gravity is about 13·6, which when solid becomes about 14·2. At a temperature of 357·25° C. it *boils*, giving a colourless vapour, but gives off vapour at much lower temperature, even below 40° C.[1] (see Condensation). Its low specific heat, high conductivity, and high boiling-point render it suitable for the construction of thermometers; its fluidity and high specific gravity for barometers. When in a very fine state of division, and a film of foreign matter interposes, the globules will not unite together, and the mercury is said to be *floured*.

It is permanent in air, oxygen, etc., at ordinary temperatures, but when heated near its boiling-point in air it oxidises, forming red oxide of mercury. This is reduced to metal, with the separation of oxygen at a somewhat higher temperature. It is attacked by chlorine and ferric and cupric chlorides.

It is unattacked by hydrochloric acid, and but slowly by sulphuric acid, unless hot and concentrated, when sulphurous acid gas is evolved and sulphate of mercury formed. Strong nitric acid rapidly dissolves the metal, but when dilute and cold has little action. Mercury compounds are readily decomposed by iron, copper, and other metals.

Mercury combines directly with sulphur, producing mercuric sulphide, or vermilion. It is prepared by heating mercury and sulphur together in an iron pan, with constant stirring, when a black brittle mass is produced. This is introduced at intervals into long, upright, iron retorts, or tall earthen jars, the lower parts of which are heated to redness. The sulphide volatilises and condenses in a crystalline form in the cool upper parts. This deposit is *red*, and is ground, levigated, and dried. It is the *vermilion* of commerce.

Amalgams.—Mercury attacks and dissolves most metals, forming liquid alloys when the mercury is in excess. If the excess is removed by squeezing through chamois leather a semi-solid amalgam is generally obtained. The remainder of the mercury may be expelled on heating, and the dissolved metal recovered.

[1] A gold-leaf suspended over mercury at the ordinary temperature is whitened in course of time, being attacked by the vapour evolved.

Gold, silver, zinc, tin, lead, antimony, bismuth, copper, and the alkali metals may be amalgamated by addition to mercury. Copper is best amalgamated by decomposing a salt of mercury by metallic copper, as the surface is not readily attacked by the metal. Mercurous nitrate is generally employed. Iron is not attacked directly, but iron amalgam may be obtained by the electrolysis of ferrous chloride with a negative pole of mercury.

The presence of these amalgams renders mercury less mobile, and when base metals are present, the oxidation which takes place, owing to the fine state of division of the metal in solution, causes the mercury to leave a " tail " behind it, if run down a slightly inclined porcelain tile. When pure it leaves no tail.

The amalgam with tin was used for silvering looking-glasses; amalgams with copper, tin and cadmium, silver and gold are used as tooth stoppings. The density of the copper amalgam is the same solid as plastic, to which state it may be reduced by slightly warming and working in a mortar. It is used for sealing bottles.

Metals are not readily attacked by mercury unless the surface is clean. Hence the presence of free acid aids amalgamation by removing films of oxide, etc. Sodium amalgam is often added to mercury in the amalgamation of gold and silver ores to prevent the mercury becoming " dead " and inactive by the oxidation of other metals, such as copper, etc., which may be taken up by it. Such mercury is apt to get into a finely divided state, the oxide films preventing the globules from coalescing, and it " sickens " or becomes " floured," in which case both the mercury and the precious metal it contains will probably pass into the residues or " tailings " and be lost. The sodium, by liberating hydrogen from the water present at the surface of the globules, prevents oxidation.

The silvering of mirrors was accomplished by squeezing mercury from a chamois leather bag over a sheet of tinfoil lying on a polished slab, forming a thin film of the amalgam. The carefully cleansed glass is then pushed gradually on, taking care to prevent air bubbles getting between, covered with felt and weighted. By inclining the slab and increasing the inclination from time to time, the excess of mercury is drained away and the amalgam adheres to the glass. The resulting film contains about 20 per cent. of mercury and 80 per cent. of tin. Mirrors are now silvered by chemically precipitating pure silver on the surface of the glass.

Ores of Mercury

" Native " Mercury occurs in globules in cinnabar, and amalgams of gold and silver are also found.

Cinnabar.—Mercuric sulphide (HgS) is the principal ore. It is a heavy mineral, of a vivid red colour; but some varieties are purplish. Its specific gravity is about 8. Large deposits occur at Almaden in Spain, Idria in Carniola, Bavaria, California, Chili, Peru, China, and elsewhere. Like hematite, it gives a red streak, but is volatilised by heat. The Idrian deposits have been worked about 400 years. Cinnabar when pure contains 85 per cent. of mercury, but the ores frequently contain less than 2 per cent., and are often bituminous in character. Mercury is often a constituent of fahl ore (p. 210).

Smelting, or Extraction.—The principles involved in the separation of mercury from cinnabar are very simple When heated in a current of air, the sulphur is burnt off as SO_2, and the metal volatilised.

It therefore only remains to efficiently condense the vapour. This, owing to the readiness with which the metal gives off vapour, is a matter of much difficulty.

Cinnabar is decomposed when heated with lime, sulphide and sulphate of lime being produced thus :—

$$4HgS + 4CaO = 3CaS + CaSO_4 + 4Hg$$

Iron reduces it to mercury, sulphide of iron resulting.

Idrian Furnace.—Fig. 131 shows the furnace employed at Idria. The cinnabar is placed on arches *n*, *p*, *r*, in the central chamber, over the fireplace. The larger lumps are placed in the lowest arch. The upper arch is occupied by small ore or dust, on trays, as shown, or moulded into blocks with a little clay. The products of the combustion and the SO_2 and mercury vapour are led to the condensing chambers C, of which there are six on each side, by the passages *s'*. Each chamber communicates with the next alternately at top and bottom. The greater part of the metal is condensed in the first two or three chambers. The remainder is deposited as soot or dust in the succeeding chambers. The floors of these chambers incline towards an outlet at the side, by which the condensed mercury drains away, and is carried by a channel to the locked tank in which it collects. In the last chamber the condensation is assisted by water spray or by canvas screens stretched across it, covered with wet sawdust. The furnace and condensers are about 180 feet long and 30 feet high. The charge for the double furnace is nearly 100 tons. The operation takes about a week to complete, of which five days are occupied in cooling, and only about 12 hours in distillation. About 4 tons of mercury are obtained from each charge.

FIG. 131.

In Hahner's modification of the Idrian furnace, the ore, mixed with charcoal, is fed into the central shaft from a hopper above, and the furnace works continuously. The condensing chambers are prevented from becoming overheated by covering them with iron plates and cooling by a spray of cold water. The spent ore is removed at intervals through the grate at the bottom of the shaft.

Aludel Furnace.—Fig. 132 shows the Aludel furnace in use at Almaden in Spain. The ore is placed in the chamber F, resting on perforated arch C, over the fireplace B. A quantity of spent ore or quartz is placed in the bottom, then poor ores followed by richer ones. The powdered ores are made into balls and placed on the top. A

wood fire is first made in B, and the whole thoroughly heated. The fires are then withdrawn and air admitted. In passing through the grate, spent ore, etc., at the bottom, it becomes heated, and calcines and reduces the cinnabar. The vapour and gases pass out by the passages L, and through rows of "aludels" resting on sloping masonry

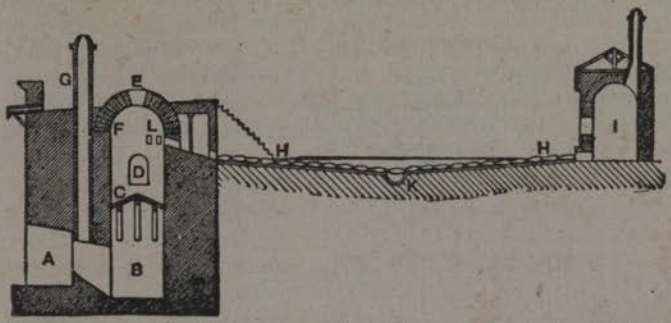


FIG. 132.—B, fireplace; C, perforated arch; F, ore chamber; D E, charging openings; G, chimney for fire; L, openings to aludels; H, aludels; K, mercury gutter; I, condensing chamber.

roofs or benches. The aludels are earthenware, pear-shaped condensers (Fig. 133) 16 inches long; the neck is $4\frac{1}{2}$ inches, the wider end about 7 inches, and the middle 11 inches in diameter. These are fitted together and luted with clay. The middle ones have a hole on the under side which permits the condensed mercury to drain into the trough K, by which it is conveyed away. From the aludels the vapours pass into the chamber I, from which they escape by the small chimney. The operation lasts about 24 hours, and the cooling down three or four days. The condensation in both these furnaces is imperfect.

FIG. 133.

Muffle, or Retort, Furnaces are used for reducing the pure "fines" (small ore), and the fume which collects in the condensers nearest the ore chamber, which consists mainly of sulphide and sulphate. From 10 to 20 per cent. of quicklime is added and the mixture made into bricks. These are heated and the vapour condensed in iron tubes dipping under water.

The Alberti Furnace is a long-bedded, reverberatory furnace, the flues of which consist of large water-cooled iron pipes. Poor ores are treated in these furnaces, but the acid vapours attack the iron.

Channel Furnaces.—The beds of these furnaces are steeply inclined planes divided into channels down which the ores trickle, being roasted by an ascending current of air and hot gases from a fire situated at the bottom of the incline. The vapours are led into condensers.

Shaft Furnaces are extensively employed. These furnaces work

continuously. The ore chamber D (Fig. 134) is cylindrical in form, standing on a hexagonal base. Three fireplaces C, with ash-pits, etc., communicate with the chamber on alternate sides of the hexagon. Below the fireplaces the chamber contracts and the calcined ore is withdrawn through openings at the side. The top of the chamber is closed by a cup-and-cone arrangement, the cup being covered by a gas-tight cover, which is always in position before the cone is lowered to admit the charge, thus preventing escape of vapours. The gases are led away by inclined iron pipes to condensers. Peep-holes, for the inspection of the furnace, are also provided. The chamber is 19 feet from base of cone to bell, and 6 feet wide. It roasts about 10 tons per day. In starting, the shaft is filled to the level of the fireplaces with spent ore, and then to within 3 feet of the top with ore mixed with 1 or 2 per cent. of coke or charcoal. The fires

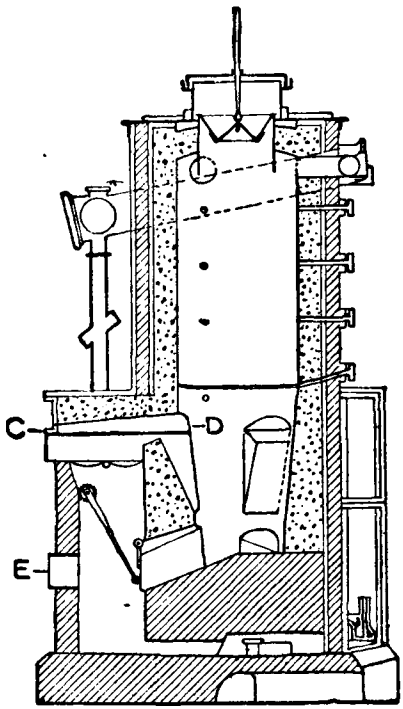


FIG. 134.—Californian furnace.

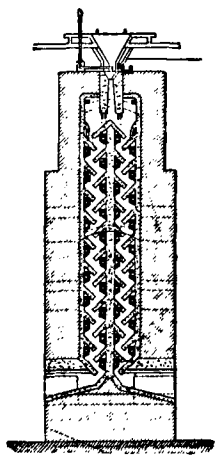


FIG. 135.

in C are lighted, wood being used as fuel, and the whole furnace heated to full redness. Some spent ore is then removed through E and fresh ore admitted from the top. Fresh additions are made about every two hours.

Hüttner and Scott's furnace for the continuous treatment of fines is shown in Fig. 135. The fine ore is fed in from the hopper at the top of the chamber, on to a series of sloping shelves, and passes in a zigzag fashion down the furnace, being turned over and over in its descent. The furnace is 27 feet high, 25½ inches wide, and 11 feet

6 inches long. At one end is a fireplace supplied with hot air heated in iron pipes placed in the condensing chambers. The fire gases, mixed with hot air, are admitted to the ore chambers by a series of openings at one end, under each shelf, and pass away to the condensers by corresponding openings at the opposite end of the furnace. The furnace treats about 1½ tons per hour, and the spent ore is removed at intervals.

A continuous retort furnace erected by the "El Pouvenir" Company in Spain, is shown in Fig. 136.[1] The retorts A are of cast iron, and are supported above a fireplace B. The retort inclines upwards, and communicates with the condensing apparatus C by a flue as shown. A hydraulic exhaust injector D draws the vapours through the condenser and permits of the lower end of the retort

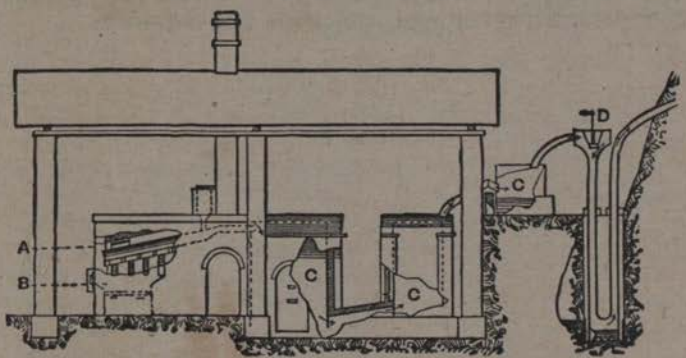


FIG. 136.

being opened to remove a portion of the charge without escape of vapour. The ore is fed in at the top, about ½ cwt. every hour and a half, giving an average of ¾ ton per retort per day. Rich ores are mixed with lime. Two large condensing chambers are provided. From the second they pass into a smaller chamber containing water, and then to the exhaust.

In shaft furnaces at the same works the hydraulic exhaust is also employed. The fireplace is placed below a perforated arch, as at Almaden, but the top is provided with charging apparatus, and the ore is discharged after calcination through openings at the side.

The **condensation of mercury** offers a difficult problem. In calcining furnaces of all types, the large volume of gases to be cooled (products of combustion of fuel, nitrogen of the air, sulphur dioxide, and mercury vapour), and the ease with which mercury gives off vapour, render its perfect recovery difficult. The gases often contain less than 1 per cent. by volume of mercury vapour. Except in the condensers nearest the ore chambers, iron cannot be used on account of the acid liquors (H_2SO_3 and H_2SO_4), which condense when sufficiently cool. Other metals cannot be used as they are attacked by mercury.

It is therefore necessary to employ large condensers, as at Idria, to slow down the

[1] *Journal Soc. Chem., Ind.*, 1890, p. 93.

current to completely cool them, and to admit the vapour as near the boiling-point as possible. With furnaces working continuously, auxiliary cooling appliances, such as earthenware or iron pipes, with or without water cooling, are necessary. Glass chambers in wooden frames have been largely adopted for gases comparatively cool, communicating alternately at the top and bottom. Mercurial vapours are highly posionous, producing salivation.

Purification of Mercury.—Commercial mercury often contains lead, zinc, bismuth, and other impurities. The presence of these may be detected by allowing it to run down a white tile. If impurities are present, the metal leaves a tail. Mercury is purified by squeezing through chamois leather and subsequent re-distillation. It may also be purified by exposing it in a thin layer to the action of dilute nitric acid, mercurous nitrate, or ferric chloride solution. The impurities are dissolved together with some mercury. It comes into the market in screw-necked iron bottles, containing $\frac{1}{2}$ to $\frac{3}{4}$ cwt. each.

CHAPTER XV

SILVER

Physical Properties.—This metal is characterised by its whiteness and brilliant lustre. It is somewhat softer than copper, but harder than gold. It is exceedingly malleable, being in this respect only inferior to gold, with which it may be alloyed without seriously impairing the malleability of that metal. It is highly ductile, and has a tensile strength of 14 tons per square inch. Its specific gravity is 10·5. It is the best conductor of heat and electricity. At about 955° C.[1] it melts, and at high temperatures is sensibly volatile. In the electric furnace it boils and distils.

Chemical Properties.—The metal is unoxidised when heated in air or oxygen, but molten silver *dissolves* about 22 times its volume of oxygen, which is given out on solidifying, the metal often being projected from the surface in curious growths. This phenomenon is known as " spitting," and does not occur if the metal is impure. The metal contracts on solidifying. Silver oxide (otherwise produced) is decomposed by heat into silver and oxygen.

Silver combines readily with sulphur, forming silver sulphide (Ag_2S), a soft, dark-grey, fusible body. The blackening of silver when exposed is due to the formation of this body by sulphur compounds in the atmosphere. This compound is also precipitated by adding sodium or other soluble sulphide to solutions containing silver.

Sulphide of silver roasted in air is decomposed, sulphur dioxide and silver resulting. When calcined at low temperatures in admixture with sulphides and sulphates of other metals sulphate of silver is produced. The sulphate is also produced by heating silver with strong sulphuric acid or bisulphate of soda. Silver sulphate is soluble in water containing free sulphuric acid, and is decomposed by heat, metallic silver resulting. Silver sulphide is converted into chloride by the action of ferric, cuprous, and cupric chlorides.

Silver combines directly with chlorine, forming silver chloride, which is not decomposed by heat. This compound is also produced when hydrochloric acid, or a soluble chloride is added to a silver solution, and by roasting the sulphide with salt in the presence of moist air. It is insoluble in acids,[2] but dissolves in strong brine (sodium chloride) and other chlorides (especially ferric and cupric

[1] The melting-point in air is 955° and in a reducing atmosphere is 962°. This is closely connected with the solubility of oxygen in silver.

[2] AgCl is somewhat soluble in hydrochloric acid. The strong acid dissolves 1 in 200 parts, and when diluted with an equal bulk of water 1 part in 600.

chlorides), in sodium thiosulphate (forming $Ag_2S_2O_3 2Na_2S_2O_3$, if the sodium salt is in excess), in potassium cyanide (forming AgCN.KCN), and in ammonia. It fuses at a red heat, and is volatile at high temperatures.

Chloride of silver is reduced by "nascent" hydrogen, mercury and other metals, and by fusion with carbonate of soda.

$$AgCl + H = Ag + HCl$$
$$2AgCl + Na_2CO_3 = 2NaCl + CO_2 + O + 2Ag$$

Silver is deposited from solution in the metallic state by zinc, copper, iron, and other metals, and cuprous oxide.

Sulphuric acid dissolves it when heated, forming sulphate.

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2$$

Nitric dissolves it readily, silver nitrate being formed.

$$6Ag + 8HNO_3 = 6AgNO_3 + 2NO + 4H_2O$$

Hydrochloric acid has no action upon it.

Silver nitrate ($AgNO_3$) is a white solid, soluble in water. It crystallises in flat tabular crystals. It is fusible without decomposition, but at a higher temperature, much below redness, it gives off oxygen and forms $AgNO_2$. At a red heat it is decomposed, yielding metallic silver.

This is made use of in the separation of silver and copper nitrates. The latter decomposes at a much lower temperature than the silver nitrate, and by careful heating may be resolved into oxide, leaving the silver nitrate unaltered. When a sample, treated with water, gives no blue colour on the addition of ammonia, the mass is boiled with water, to dissolve the silver nitrate, and filtered from the insoluble copper oxide. Boiling the mixed nitrates with freshly precipitated silver oxide also throws down the copper as oxide.

Large quantities of nitrate and sulphate of silver are produced in parting silver and gold.

Alloys.—Silver is too soft for use in the pure state, and is hardened by alloying it with copper. English sterling silver, "standard silver," consists of an alloy of 925 parts of silver per 1,000 alloyed with 75 of copper. This is equivalent to 11 ozs. 2 dwts. of silver per lb. *troy*. Alloys which contain more silver per lb. are described as "better," and those containing less as "worse" than standard. The Indian rupee, 11 ozs. 8 dwts. per lb., is 6 dwts. better, and the French standard alloy contains 10 ozs. 16 dwts. only, and is described as 6 dwts. worse.

The degree of purity is now usually expressed in parts of silver per 1,000; thus "900 fine" implies that the alloy contains 900 parts of fine silver and 100 of alloy per 1,000.

Note.—Alloys used for British coinage were formerly sterling silver. Since 1920 other alloys have been used. From 1920–22 an alloy of 50Ag, 40Cu, 10Ni, was used. 1923–27, 50Ag, 50Ni. From 1928, 50Ag, 40Cu, 5Ni, 5Zu.

Frosted Silver.—Silver is frosted by heating silver alloyed with copper in air. The *copper* oxidises, and the oxide is dissolved off with sulphuric acid or ammonia, or by boiling with cream of tartar and salt. This leaves a "dead" surface consisting of finely divided silver.

Oxidised Silver.—This effect is produced by treating the silver with a soluble sulphide, such as sulphide of potash, and is due to the films of silver sulphide formed.

Stainless Silver is rhodium plated. Beryllium oxide films electrolytically formed are also said to be effective.

Ores of Silver.

"Native" silver occurs associated with ores of the metal; with gold, in electrum; with mercury, in amalgam (see p. 33).

Silver Sulphide (Ag_2S)—Argentite—occurs as a soft, malleable greyish-black substance, which is readily fusible. It contains 87 per cent. of silver. Deposits containing it in a state of purity occur in Norway, Hungary, Saxony, Bohemia, Mexico, and the United States. It is the principal ore of silver.

Horn Silver—Silver Chloride (AgCl)—is found in South America. The bromide and iodide also occur.

Pyrargyrite.—Dark-red silver ore is a sulphantimonide of silver ($3Ag_2S.Sb_2S_3$) found in Mexico, South America, Transylvania, and elsewhere. **Proustite**—light-red silver ore—is a sulpharsenide ($3Ag_2S.As_2S_3$). **Stephanite** is another mineral of the same class.

Polybasite and **Argentiferous Fahl Ore** are compounds of copper, silver, arsenic, and antimony sulphides. The latter often contains other metals also.

Silver occurs in the ores of many other metals, probably as sulphide. Lead, zinc, and copper ores often contain it, and small quantities occur in iron pyrites and mispickel (arsenical iron pyrites). The production of silver from these sources is nearly one-half of the total extracted.

Extraction Processes.—The high price of silver permits of poor ores being treated and the adoption of more costly methods. Hence chemical methods, preceded by careful mechanical preparation, are often followed.

The treatment of silver ores proper may be divided into—

Amalgamation processes.
Wet processes.
Smelting with lead, or lead ores.
Smelting with copper ores.

Amalgamation Processes include those in which the silver is obtained as an amalgam with mercury, from which it is recovered by distillation and volatilising the mercury. They may be divided into "floor," "barrel," and "pan" amalgamation processes. If not present as free silver or as chloride the first step of the process is to convert the metal into chloride.

Floor Amalgamation.—In the "patio" process, still followed in Mexico and South America, the ores are hand-picked, and then contain some 80 ozs. of silver per ton, as native silver, chloride, and sulphide. Base ores containing large amounts of foreign sulphides are unsuitable for treatment by this process. The ore is first reduced to a fine state of division by stamping or grinding.

The *quimbalete* consists of a large boulder lashed to the middle of a long pole, rocking on a flat stone, worked by men sitting astride the ends of the pole, and working see-saw fashion, the ores being thrown under the boulder.

The *trapiche* is a large stone wheel, 6 feet in diameter and 5 feet across; the axle on which it revolves is attached to a perpendicular shaft driven by a horizontal water-wheel on the top. The wheel travels round a stone track, and the ores are gradually crushed.

The *arastra*, for fine grinding, is a circular trough paved with hard stone. In the centre is an upright post to which projecting arms are attached. Heavy stones are lashed to these, by thongs of raw hide, and they are dragged round by mules attached to the ends of the arms, which project over the edge of the trough. Water is added, and, if much free silver or gold is present, a little mercury, to amalgamate them. The ore is thus reduced to mud.

The *Chilian mill* for grinding ores is in principle like an ordinary mortar-mill.

The operations are conducted as follows:—(1) The mud is taken to the amalgamating floor, or patio—a paved court—and spread out in a layer 6 inches to a foot thick. Some 3 to 5 per cent. of salt is added and well trodden in by mules for several hours, after which the heap is allowed to rest.

(2) Next morning a quantity of roasted copper pyrites—*magistral*[1]—is scattered over the heap, and some mercury. This, after mixing with shovels, is well trampled in; the turning over and trampling are repeated every other day for some days.

(3) Mercury to the extent of some 5 or 6 times the weight of silver present is sprinkled over the heap from canvas bags, and trampled in. If much antimony and arsenic, or other foreign sulphides are present, a hot solution of copper sulphate is added, together with copper precipitate (finely divided copper) (see p. 234), and thoroughly incorporated.

(4) After a further rest with repeated tramplings, a final addition of mercury is made to collect the amalgam, and after mixing, the stuff is conveyed to tanks where it is stirred up with water, and the heavy amalgam settles out. The earthy matters are carried away by the water current.

The amalgam is treated in the ordinary manner (see p. 273).

In this process a series of complicated reactions occurs. Copper chloride is formed by the reaction of the salt and copper sulphate.

$$CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4$$

This attacks the metallic silver, thus:

$$2CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2$$

This cuprous chloride, which is soluble in the excess of salt employed, reacts on the sulphide of silver and converts it into chloride.

$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S$$

Some free sulphur is also separated, probably thus:

$$Ag_2S + 2CuCl_2 = Cu_2Cl_2 + 2AgCl + S$$

or $2Ag_2S + 4Cu_2Cl_2 + 6O = 2(CuCl_23CuO) + 4AgCl + 2S$

[1] This contains both copper and iron sulphates, and plays a material part in the reactions which occur.

The above reactions in some degree represent the chlorination, but the changes are very obscure. The silver chloride is decomposed by mercury, thus:

$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag$$

the metal being dissolved by the excess of mercury. The operation occupies from 2 to 7 weeks.

Note.—The addition of copper precipitate is to ensure the reduction of the cupric salt to the cuprous state, or it will attack the mercury, forming calomel,[1] and will thus increase the consumption of mercury.

$$2CuCl_2 + 2Hg = Hg_2Cl_2 + Cu_2Cl_2$$
$$2CuCl_2 + 2Cu = 2Cu_2Cl_2$$

Formerly lime was added, to precipitate the copper, if in excess; but this hinders the chlorination by forming an inactive chloride.

Barrel Amalgamation was formerly practised at Freiberg. The chlorination of the metal is effected by roasting the ore with salt as described (pp. 234 and 276). The roasted ore is next put into barrels capable of holding about a ton, supported horizontally on trunnions. Water is added to make it into a stiff paste (pulp), some $1\frac{1}{4}$ to $1\frac{3}{4}$ cwt. of sheet-iron scrap added, and the barrels revolved for several hours. The chloride is reduced by the iron, thus:

$$2AgCl + Fe = FeCl_2 + 2Ag$$

Mercury is then added to amalgamate the reduced silver, and the barrels again revolved some 16 hours. The contents of the barrels are then thinned by the addition of water, the amalgam collected together by slow revolution, and run off by a plug in the side. A little fresh mercury is added to collect any residual metal, and the barrels again revolved. This is run off as before. The residues are run into settlers and agitators—tanks with a current of water flowing through—by which the light matters are carried off and the amalgam (if any) sinks.

In the Krolinke[2] process, formerly in use at Benton, the roasting with salt is dispensed with. The chlorination of the silver is effected by an addition of cuprous chloride and salt. The cuprous chloride is prepared by boiling copper sulphate with salt and copper, or in other ways. The barrels may be arranged vertically or horizontally, and steam is blown in to heat the contents. Metallic copper is employed to reduce the silver, and the amalgamation with mercury takes pace, as before. The loss of mercury is greatly reduced, calomel not being formed. Aaron states that it can be brought as low as 2 lbs. per ton. Iron borings are sometimes used for the reduction. Base ores can be treated by this process, a yield of 80 to 95 per cent. being obtained.

In both these processes there is considerable loss of mercury by "flouring"—that is, the mercury is broken up into fine particles which will not coalesce to form a globule, and are carried off and lost. The addition of a little sodium amalgam is made to prevent this.

[1] The white insoluble mercurous chloride.

[2] *Iron*, Nos. 93 and 94.

Kettle Amalgamation (Cazo Process).—The ores treated by this process are mainly chlorides, bromides, and iodides. The ore is ground to a pulp in the mill, or arastra, and transferred to kettles with bottoms made of copper. From 5 to 10 per cent. of salt is added, and the mass heated with continual stirring. Mercury is added, and the heat is continued for some hours, till amalgamation is complete. The mass is then thinned with water, and the amalgam collected as before. The chloride, etc., is decomposed by the copper,

$$2AgCl + 2Cu = 2Ag + Cu_2Cl_2$$

yielding silver and cuprous chloride. This, in the presence of salt, reacts to some extent on the sulphides, after the manner of the "patio" process, but sulphide ores generally retain enough silver to be subsequently treated on the "floor."

Pan Amalgamation.—The foregoing methods have generally given way to treatment in pans, a great saving in time being effected

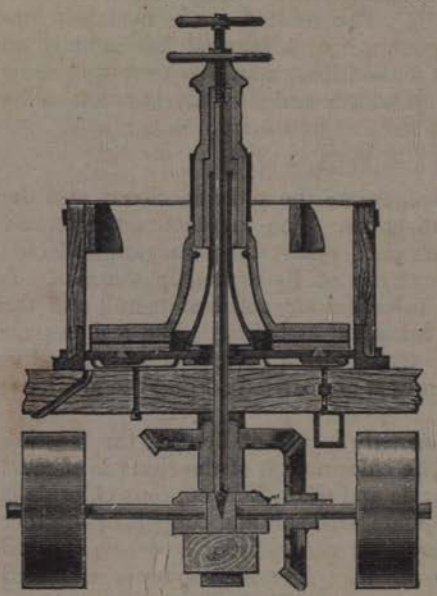


FIG. 137.—Amalgamating pan.

The pans employed in these processes vary somewhat in construction. One form is shown in Fig. 137. It consists of a cast-iron pan some 5 feet in diameter, with a steam-jacketed bottom. Up the centre a hollow pillar rises, through which a shaft passes. To this the cast-iron muller is attached in a manner which permits of its being raised or lowered to any desired height by means of the hand-wheels on top. The crushed ore is ground between the flat faces of the muller and the bottom of the pan, motion being communicated by the bevel-wheel gearing under the bench on which the pan rests. Steam is admitted to keep the contents hot. A plug is provided for running off the pulp after amalgamation.

Instead of iron sides, wooden staves hooped with iron are employed, and copper bottoms and linings are sometimes employed.

Two methods of treating the ores are followed. In one they are treated direct, and in the other they undergo a previous roasting with salt to chlorinate the silver.

In the *direct* process the ore is broken in a "stone-breaker,"

or " ore-crusher " of the Blake type, A (Fig. 138), passes to a stamp battery B, and is crushed " wet "—that is, with a supply of water (see Gold, p. 290), a 30-mesh screen being employed. From the

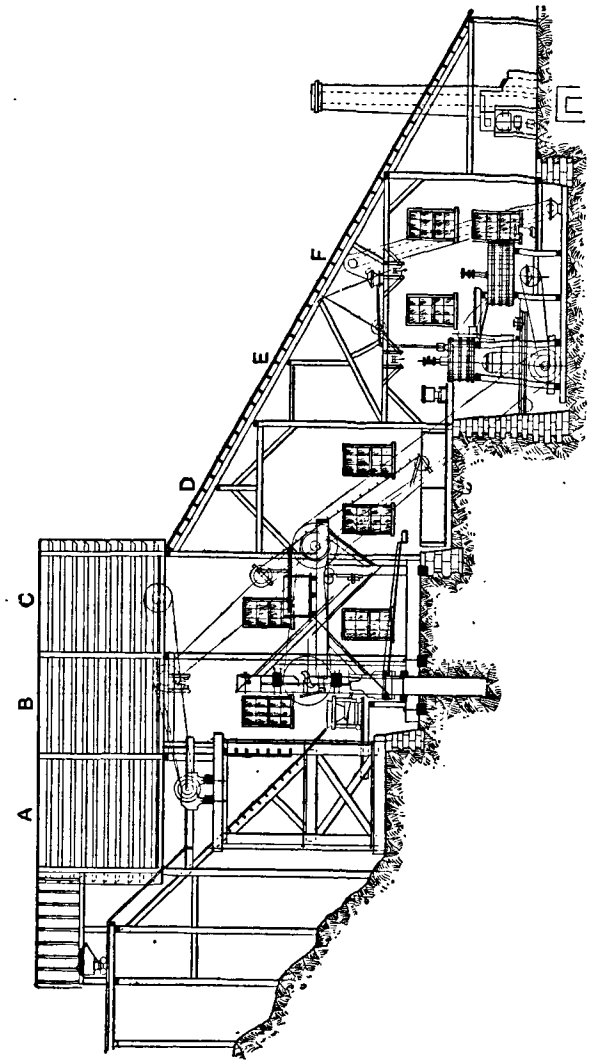


FIG. 138.—Wet-crushing silver-mill.

battery the crushed ore passes over the amalgamated copper plates C to catch any free gold present, and then to the tanks D, in which the mud settles.

The mud (pulp) is charged into the pans E, water added to a pasty

consistency, and the muller lowered and revolved at the rate of 80 to 100 revolutions per minute. Salt and copper sulphate are also added, and the temperature is maintained at about 90° C. This grinding is continued some 3 or 4 hours. The pulp will then pass through an 80-mesh sieve. About 10 or 15 per cent. of mercury is then added, and the muller, somewhat raised, is again revolved for 2 or 3 hours, to thoroughly incorporate the mercury. The pulp is then thinned by the addition of water, and run off by the plug into the settler F, which resembles the amalgamator save that the muller is replaced by a stirrer (Fig. 139) which makes some 10 revolutions per minute. Here the amalgam settles out. The mud is drawn off, by opening the holes in succession, into another settler—the agitator—and then passed on to "frue vanners," or otherwise treated, for the separation of the pyrites, etc. (concentrates), which often carry gold, while the light stuff is washed away.

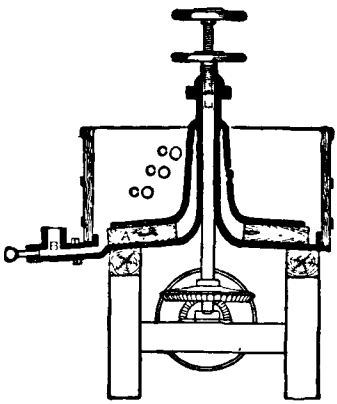


FIG. 139.—Settler.

In amalgamation processes preceded by roasting the ores are crushed "dry."

In "dry" crushing, the ore, after being broken, is dried, a rotary furnace being employed. The dried ore is stamped, and the crushed ore falling through the screens is conveyed away by means of Archimedian screws, travelling belts, or elevators. Fig. 140 shows a "dry" crushing mill. The powdered ore is next mixed with about 20 per cent. of salt, and roasted. Generally revolving furnaces of the Brückner type (Fig. 39) are employed. Stetefeldt calciners (Fig. 41), and multiple-bedded reverberatory furnaces are also employed. This roasting occupies about 8 hours. The ore is then transferred to the amalgamators and treated as before. The yield by this treatment is much greater than in wet crushing, but the items of labour and fuel consumption are increased, while the output of a plant is seriously diminished.

The loss of mercury is about 2 pounds per ton of ore treated. It is customary to add a little sodium or zinc amalgam, to keep the mercury from *flouring*, the hydrogen evolved keeping the mercury bright and *lively*, and preventing the formation of a film on the small globules, which prevents them from coalescing. Potassium cyanide, in small quantities, is often used for the same purpose. In wet crushing, mercury is also introduced into the mortar-box to retain gold.

In the roasting of *dry-crushed* ores with salt, there is a liability to form gold chloride, which is soluble, and will be lost if not completely decomposed in the pans.

In "wet" crushing, the sulphide of silver in the ore seems to be partially decomposed by the iron of the pan during amalgamation, with the formation of sulphide of iron, assisted by the cuprous chloride, produced when salt and copper sulphate are added.

The *best grinding* is secured with a thin pulp, and the *best amalgamation* with thick pulp, which prevents the mercury from settling out. It is usual to add *residues* to thicken the pulp prior to adding mercury. It is soft enough if the muller will turn in it.

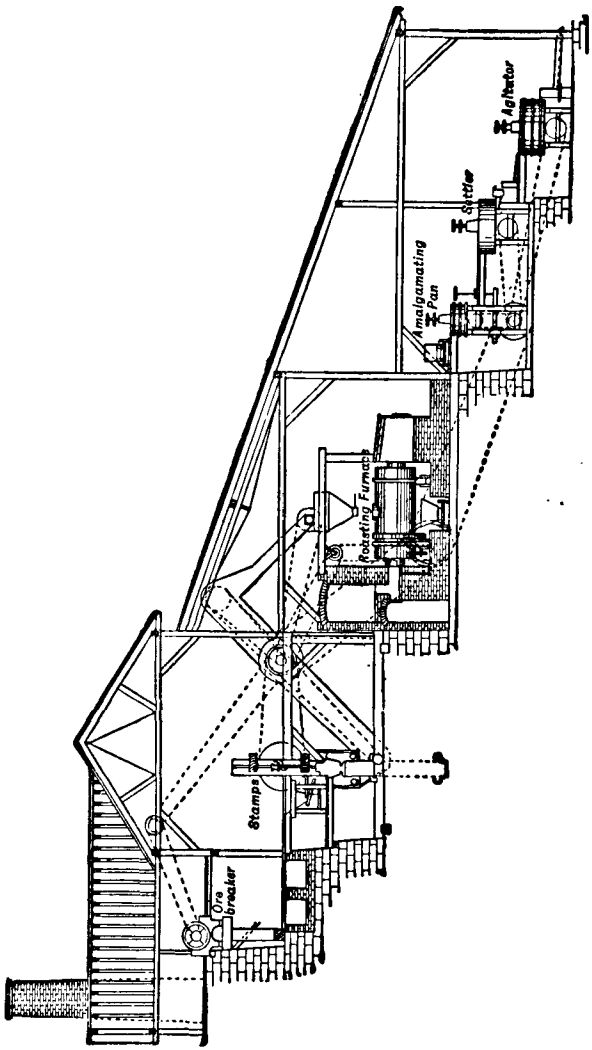


FIG. 140.

Treatment of Amalgam.—The amalgam from the settlers and agitator is often transferred to a smaller "clean-up" pan, and stirred with water to free it from heavy particles.

It is then strained through canvas bags, or squeezed through wash-leather, or in cylinders, the ends of which are made of wood cut across

the grain, by hydraulic pressure. The excess of mercury which is thus removed is used again. It contains silver, but this is recovered in the subsequent working. The pasty amalgam which remains is then "retorted" to expel the mercury. One form of retort is shown in Fig. 142. The amalgam is put into the crucible, which is of iron, the head adapted, and the mercury as it distils off is condensed by the water-cooled tube. The crucible is coated with limewash.

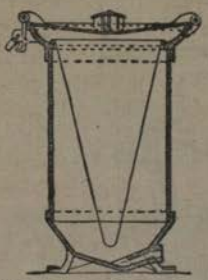


FIG. 141.—Amalgam safe, with strainer.

The porous mass obtained is subsequently melted down in crucibles, and cast into bars weighing about 1,000 ozs. The crude bullion contains bismuth, antimony, copper, zinc, arsenic, etc. It is subsequently refined. This is partially effected by exposing the surface to the air while molten, and permitting the impurities to oxidise, the scum of oxides being scraped off. It is afterwards refined by cupellation.

Wet processes.—The wet methods of extraction formerly practised depended on the solubility of chloride and sulphate of silver, the

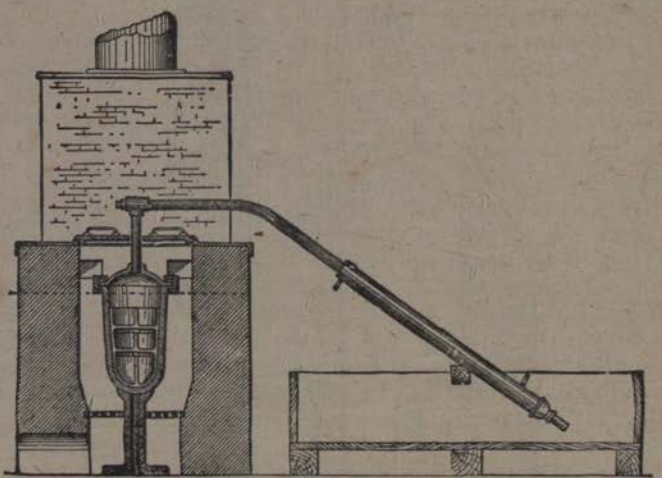


FIG. 142.—Retort.

former in solutions of common salt and other chlorides and in thiosulphate of soda, and the latter in water more or less acidified. These processes have been almost entirely superseded by the simpler methods of extraction by cyanides of potassium and sodium. A brief résumé of the older processes is given.

Sulphating roasting.—*Ziervogel Process.* This process or some modification of it was formerly largely followed for the treatment of

copper and other mattes and for the preliminary treatment of bottoms (see p. 217) or other argentiferous coppers, in addition to its application to certain ores containing silver.

It depends on the conversion of the silver into sulphate by calcining under favourable conditions. When a mixture of sulphides is calcined the chemical changes that take place depend mainly on (1) the basicity of the oxide formed, (2) the atmosphere of the furnace, (3) the temperature.

If the oxide of the metal resulting from the calcination be highly basic, the sulphur dioxide in the presence of free oxygen, and probably moisture, will be fixed as sulphate in proportion to the basicity of the oxide and the stability of the sulphate when heated. Thus:

$$\begin{aligned} FeO + SO_2 + O &= FeSO_4 \\ CuO + SO_2 + O &= CuSO_4 \\ ZnO + SO_2 + O &= ZnSO_4 \\ PbO + SO_2 + O &= PbSO_4 \\ CaO + SO_2 + O &= CaSO_4 \end{aligned}$$

There is a *remote* possibility of the sulphate being formed directly. Sulphates which undergo decomposition to oxide when heated liberate sulphur trioxide, which may (1) be immediately dissociated, (2) serve as a powerful oxidising agent, or (3) unite at once with a base whose sulphate is stable at the temperature, thus increasing the proportion of sulphate of that metal produced. This may extend in extreme cases—a powerful base and little sulphur—to the fixation of the whole of the sulphur as sulphate.

Sulphur trioxide in the presence of moisture may behave like sulphuric acid and oxidise and combine with the oxide formed if the sulphate is stable at the temperatures.

Hence, in calcining a mixture of sulphides at a gradually increasing temperature, a series of progressive changes may take place, in addition to the main effects of eliminating sulphur and the formation of sulphates and oxides.

The sulphates of iron, copper, silver, zinc, lead, and calcium are decomposed by heat in the order named. When a mixture of the sulphides is calcined, part of the sulphide in each case (except silver) is converted into oxide and this partially into sulphate. As the temperature rises the decomposition which occurs increases the amount of those sulphates which are stable at that temperature. Thus in a mixture of iron and copper sulphides the decomposition of the iron sulphate tends to produce an increased amount of copper sulphate.

$$\begin{aligned} 2FeSO_4 &= Fe_2O_3 + SO_2 + SO_3 \\ CuO + SO_3 &= CuSO_4 \\ CuO + SO_2 + O &= CuSO_4 \end{aligned}$$

The ferric oxide (Fe_2O_3) formed acts as a catalyst and assists in the conversion of SO_2 into SO_3. This is also assisted by the brick-

work of the furnace and siliceous matter in the ores. The presence of moisture is probably necessary. This applies generally.

Sulphide of silver does not form a basic oxide during calcination, but the sulphate is stable at higher temperatures than copper sulphate. When calcined the sulphide yields metallic silver. In a matte this would be in a very fine state of division and easily attacked by the sulphur trioxide from the decomposing sulphates of iron and copper.

$$2Ag + 2SO_3 + nH_2O = Ag_2SO_4 + SO_2 + nH_2O$$

By controlling the temperature almost complete decomposition of the iron and copper sulphates may be secured, while the silver sulphate is unaffected.

The presence of zinc and lead oxides resulting from the sulphides present or the presence of lime would seriously affect the attack of the silver by forming sulphates which have no effect. This should also be noted in connection with the Percy-Patera and other similar processes, as the amount of these metals passing into solution is of importance, determining either the method of working or the purity of the silver sulphide precipitates obtained.

From the above the function of iron sulphate sometimes added to oxide of copper for sulphating will be evident.

Chloridising roasting, as followed in the Augustin, Percy-Patera, Russell, and other processes, has for its object the conversion of the silver into chloride.

Common salt is the usual source of the chlorine. The transference may be effected in various ways.

(1) By the action of free chlorine, generated thus—

(*a*) $2NaCl + O + SiO_2 = Na_2SiO_3 + Cl_2$

(*b*) $2HCl + O = H_2O + Cl_2$

(2) Or by the action of hydrochloric acid gas, produced thus—

$$2NaCl + H_2O + SiO_2 = Na_2O.SiO_2 + 2HCl$$
$$2FeSO_4 + 4NaCl + 2H_2O + O = Fe_2O_3 + 2Na_2SO_4 + 4HCl$$

the moisture being present in the atmosphere of the furnace;

(3) By the action of chlorides of copper and iron produced by the reaction of sulphates on the salt added.

$$CuSO_4 + 2NaCl = Na_2SO_4 + CuCl_2$$
$$2CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2$$

The Cyanide Process.[1]—The application of the MacArthur-Forrest process of gold extraction by solutions of potassium cyanide has been adapted to the extraction of silver.

Cyaniding for Silver.—The recovery from finely divided ore containing the silver as sulphide and chloride amounts to 80 to 95 per cent., but metallic silver is only acted on very slowly, and its

[1] All processes for "wet" extraction of silver from silver ores have been largely replaced by cyanide extraction.

malleability prevents its reduction to a fine state of division in milling.

In carrying out the process it is necessary to secure satisfactory concentration, to separate metallics as completely as possible, the earlier in the process the better, and to separate slimes and sands for separate treatment.

Note.—Slimes includes all material that will pass a 200-mesh sieve. Most of it will pass a 300-mesh.

The stronger cyanide solutions employed make the greatest possible economic reduction in bulk necessary to reduce losses. Hand picking to remove rich material is followed by an elaborate crushing and concentrating campaign. Crushers, stamps, jigs, and Wilfley or other concentrating tables are used to remove the poorest portions of the ore. At every stage slimes are recovered by settling in Dorr thickeners or other devices as they are partly produced from the soft and rich material. All slimes pass to the special plant for separate treatment.

In cases where it is possible the ore is graded and the rich and poor portions concentrated separately, all the slimes being mixed. The preliminary concentration may separate 60 to 70 per cent. The metallics of the rich mineral are recovered from the rich material and from concentrates of both grades after prolonged fine grinding —22 to 30 hours—in tube or other mills. When much silver is present —as at Cobalt—calcium hypochlorite and caustic soda are added as oxidising agents in the mill. The grinding flattens the silver and makes it flakey. It is separated in classifiers, and after roasting, fluxed, melted, and refined.

The pulp after removal of the metallics is settled, and washed free from chlorides prior to cyaniding. Elaborate plant of every description for crushing, concentrating, washing, and filtering is employed.

At Cobalt in Canada the final concentrate may be not more than 2 per cent. of the original ore treated. The slimes may total 60 per cent.

Treatment of Slimes.—They are allowed to settle and further dewatered by vacuum filtration till only 25 per cent. of water remains. The mud—pulp—is transferred to large tanks, 30 feet by 10 feet, capable of treating 80 to 85 tons, provided with agitating appliances for cyanide treatment. About 2 tons of solution per ton of slime is employed. This solution contains about 0·25 per cent. of cyanide, and the ore is agitated from 48 to 72 hours.

The liquor is drawn off at the end of the treatment, filtered, and clarified. Sodium sulphide is added to precipitate the silver and regenerate the cyanide, in tanks fitted with agitators similar to the treatment tanks. The sulphide is recovered by filtration through filter presses, the solution going back to storage tanks.

Treatment of Sands—Concentrates.—After removing metallics the pulp is settled, washed free from chlorides, and dewatered by

filtration. It is transferred to tanks and treated with 0·5 per cent. cyanide solution, the solution being precipitated after filtration with sodium sulphide as above and filter-pressed. The recovery may reach 95 per cent. of the silver present.

Treatment of Silver Sulphide Precipitates.—The sulphide collected in the filter presses is thoroughly agitated in a tank with caustic soda solution. This mixture is pumped continuously through a revolving cylinder containing aluminium in massive form such as ingots, the silver sulphide is reduced by nascent hydrogen produced by the action of caustic soda on aluminium, sodium sulphide being formed. The reduction may occupy from 14 to 20 hours, and circulation is continued till tests show that reduction is complete.

$$3Ag_2S + 2Al + 12NaHO = 6Ag + 2Al(NaO)_3 + 6H_2O + 3Na_2S$$
$$2Al + 6NaHO = 2Al(NaO)_3 + 6H$$
$$6H + 3Ag_2S = 3H_2S + 6Ag$$
$$3H_2S + 6NaHO = 3Na_2S + 6H_2O$$

The silver pulp is filtered through a filter press and the solution of sulphide sent back for re-use.

After thorough washing to remove traces of soluble sulphide the precipitate, together with that removed as flake silver, is melted and refined.

The recovery of silver by cyaniding processes varies with (*a*) the form of occurrence ; (*b*) fineness of milling ; (*c*) strength of solutions ; (*d*) efficiency of agitation and filtration. In some ores it reaches 95 per cent., but may fall as low as 80 per cent.

The elaborate concentration methods followed are necessary to reduce the cyanide consumption, which is high.

Residues left in the filter after removing the cyanide solution may represent a very highly concentrated mineral product and be valuable as is the case in the Cobalt district in Canada, where they contain as much as 8 per cent. of nickel and 8 per cent. of cobalt.

Ziervogel Process.[1]

Roasting Copper Mattes.—They are first roasted to remove the greater part of the sulphur, and then ground very fine and carefully roasted at a low and gradually increasing temperature in a double- or triple-bedded reverberatory calcining furnace. The matte is first introduced on the bed farthest from the fire, and is moved forward towards the fireplace. When the iron and copper sulphates formed during the roasting are nearly decomposed—determined by boiling a sample with water and observing the colour—the material is raked out.

Argentiferous copper ores are generally run down for matte, which is thus treated.

The roasted material is then treated with water containing a little free sulphuric acid—*leached*—in wooden tanks capable of holding about 1000 gallons. From these the liquor is run into settling tanks, at a lower level, and thence into tanks containing copper, where the silver is precipitated. Two sets of precipitating tanks

[1] Now obsolete. It should be remembered that the reduction in the value of silver has made many processes uneconomical.

are usually employed, the first containing heavy copper scrap or bars, and the latter precipitate and bean shot-copper.

$$Ag_2SO_4 + Cu = CuSO_4 + 2Ag$$

The copper is recovered by throwing it down with iron in similar tanks.

The residues contain the gold, a portion of the silver (owing to imperfect sulphating), copper, and iron as oxides, lead as sulphate. If bismuth and antimony are present in the matte, more silver is retained, owing to the formation of insoluble compounds.

The residues are smelted for copper by the " best select " process. The bottoms obtained are treated by electrolysis, or in a manner subsequently described.

Augustin's Process.—This consists of roasting the material mixed with salt for the purpose of converting the silver into chloride, which is then dissolved out by brine and precipitated by copper.

In the treatment of copper bottoms, the two processes are often combined (at Freiberg, and some works in this country). The bottoms are granulated in water, and roasted to oxide, CuO, mixed with sulphur or sulphate of iron, and Ziervogelised.

The residues contain the gold and much silver, and are Augustinised. The gold passes into solution as chloride, and is, of course, precipitated by the copper. Great care is required in roasting, or the gold chloride will be decomposed by overheating, the metal remaining in the residue.

Claudet's Process was in extensive use for the recovery of silver from the cinders of iron pyrites used in vitriol manufacture, and is employed as an adjunct to the extraction of copper by Longmaid's process (p. 234). In the chlorinating roasting for copper, the silver is also chlorinated, and in the lixiviation with water is dissolved out by the excess of salt added in roasting. The leachings, after cooling and settling in tanks—during which much lead sulphate and chloride separate out—are assayed for the amount of silver they contain. A soluble iodide is then added in sufficient quantity to precipitate it as insoluble silver iodide [1]—

$$2AgCl + ZnI_2 = 2AgI + ZnCl_2$$

Care must be taken that the iodide is not in excess, or the following reaction will occur, cuprous iodide being precipitated—

$$2ZnI_2 + 2CuCl_2 = 2ZnCl_2 + Cu_2I_2 + I_2$$

and iodine liberated. The iodide is well stirred in, and the precipitate allowed to settle.

After the withdrawal of the liquor, the mud is moistened with hydrochloric acid and treated with zinc, when the nascent hydrogen reduces the silver iodide, and zinc iodide and metallic silver results.

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$H_2 + 2AgI = 2Ag + 2HI.$$
$$ZnCl_2 + 2HI = 2HCl + ZnI_2$$

During the reduction the mass is kept warm by jets of steam.

The mud, or precipitate, after reduction, contains 6 to 12 per cent. of silver, a little gold, and a large percentage of lead and oxide of zinc, with sulphuric acid, lime, etc. The lead is reduced by the action of the zinc.

Percy-Patera Process.—The solution of the chloride produced in chlorinating roasting by thiosulphate of soda, " hyposulphite," and precipitation of the silver as sulphide by sodium or calcium sulphides, was first proposed by Dr. Percy. Prior to the introduction

[1] In modern practice the precipitation with iodide has been superseded. The silver is precipitated by iron along with the copper, and is recovered in the electrolytic refining. In some cases the copper was precipitated in two stages, the first portion, containing the silver, being removed separately. Much less copper precipitate is now produced than formerly.

of the cyanide process it was the most important " wet " process for the treatment of *silver ores*.

In the American silver mills, where this process was pursued, the dried and crushed ore was chlorinated by roasting with salt.

After roasting—especially in White-Howell calciners—the ore was left for some hours in heaps, the chlorination proceeding after withdrawal from the furnace. It was then transferred to lixiviating vats, and leached with hot *water* to remove all soluble matters—zinc, manganese, copper, lead, and other chlorides—till the effluent liquor gave no precipitate with sodium sulphide. Some silver chloride also dissolves. The stronger liquors from the first leachings were run into tanks, and the silver they contained was precipitated by the careful addition of sodium sulphide. It is thrown down before the other metals present are completely precipitated. This precipitate contains about 4 to 6 per cent. of silver.

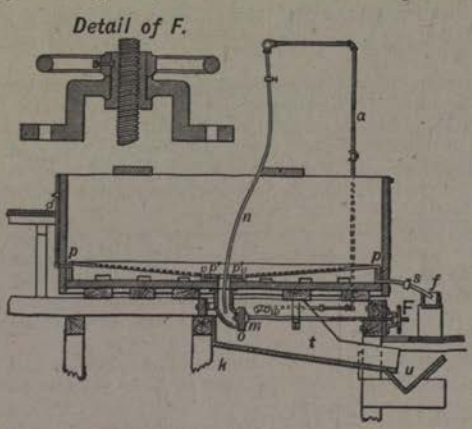


FIG. 143.—Self-sluicing lixiviation-tank. *p*, false bottom; *a*, air pipe; *s*, pipe for removal of liquor; *f*, trough leading to precipitating tanks; *m*, plug for removal of residues; *n*, sluicing pipe for ejecting residues.

The ore was then leached with sodium thiosulphate solution, of strength varying from $\frac{1}{4}$ to 1 per cent., according to the richness in silver. The solution was run by gutters under or alongside the tanks, into deep precipitation tanks holding about 1,000 gallons (5 feet diameter and 8 feet deep), sodium sulphide solution added, and silver sulphide precipitated thus—

$$(Ag_2S_2O_3{}_2Na_2S_2O_3) + Na_2S = Ag_2S + 3Na_2S_2O_3$$

The regenerated thiosulphate solution was available for use again.

Treatment of Sulphide Precipitates.—The sulphide precipitates are roasted in a furnace, and, if poor in silver, smelted with lead, which decomposes the sulphide and takes up the metal.

The lead is cupelled to extract the silver. If the sulphide is pure, after roasting, it is melted in crucibles with carbon.

In roasting, and in treatment by lead, there is great liability to loss by volatilisation and dusting. The flue dust from these furnaces assays up to 1200 ounces of silver per ton.

Formerly the silver precipitate was run down in crucibles with scrap iron, silver being liberated and iron sulphide formed. The regulus retained silver, and was re-treated. Calcium thiosulphate and calcium sulphide replaced the soda salts in the " Kiss " process.

Treatment of Base Ores.—Ores containing much lead and zinc sulphides, antimony, arsenic, and bismuth, are unsuitable for treatment by the ordinary "hypo" process, the chlorinating and leaching being rendered difficult and incomplete in the presence of those bodies. Hence some of the silver remains in the mass as sulphide, and is not removed by hypo.

This difficulty is overcome in the **Russell** process, by following or, in some cases, preceding the ordinary thiosulphate leaching with a supplementary one by the double thiosulphate of soda and copper, formed by running the thiosulphate solution through a perforated box containing copper sulphate immersed in the leaching vat just above the ore. This method is rendered necessary by the ready decomposition of the double salt on exposure, and to prevent this the tanks are closed in. The double salt has the composition—

$$2Na_2S_2O_3,\ 3Cu_2S_2O_3$$

and the reaction is—

$$2Na_2S_2O_3,\ 3Cu_2S_2O_3 + 3Ag_2S = 2Na_2S_2O_3,3Ag_2S_2O_3 + 3Cu_2S$$

The action of the *extra* solution is not rapid, and circulating pumps are employed to keep it in motion throughout the mass. Undecomposed sulphide of silver is thus dissolved out, and the silver in the residues is greatly reduced. The silver is precipitated by sodium sulphide as before.

The sulphide precipitates are, however, very impure, containing only 25 to 40 per cent. of silver. The excess of copper used in the *extra* solution is precipitated with the silver. Greater expense is entailed in refining in consequence. To obviate this, it has been proposed to treat the precipitate obtained from the *extra* solution with sodium nitrate and sulphuric acid, whereby the mixed sulphides are converted into soluble sulphates. The nitric acid fumes evolved are condensed, and the sulphur which separates used for making sodium sulphide.

The silver from the sulphate in the solution is then precipitated by copper, and the copper subsequently by iron.

In dealing with ores containing much galena, the lead sulphate and chloride formed in roasting dissolve in the thiosulphate. The lead is removed by the addition of sodium carbonate before precipitating the silver.

In zinc ores treated by this process, the zinc sulphate formed is dissolved out in the preliminary leaching with water.

In these processes, any gold contained in the ore was extracted to a large extent, and precipitated with the silver as sulphide. During the leaching it is attacked by the thiosulphate, and thus dissolved out.

The wooden tanks employed in these lixiviation processes are either round or square, well coated on the inside with tar. They are provided with a perforated false bottom covered with canvas, on which a layer of filtering material, about a foot thick, is laid. This material consists of gravel and silver sand, in layers, or of sawdust, according to circumstances. Over the top of the filter is another canvas covering.

The leaching liquor is frequently poured on the top of the ore, but sometimes is introduced by a pipe below the false bottom, and allowed to percolate upwards until the mass is soaked, to avoid air being trapped and secure uniform wetting and percolation, after which it is poured on top as usual. Below the false bottom is an opening in the side of the tank, by which the liquors are run off and carried by gutters into the settling and precipitation tanks. These, for convenience, should, if possible, be placed at a lower level. Steam-jet injectors are employed to elevate the liquors, if necessary

Silver from Lead.—Pattinson's process for the concentration of the small amount of silver occurring in lead has been noted on p. 230, and the melting with lead of the roasted sulphide precipitates obtained in the Von Patera, on p. 280. Silver ores, if pure sulphides, are

sometimes added to a bath of lead in a reverberatory furnace, much in the same manner as the poor Von Patera precipitates. The silver compounds are decomposed by the lead, and the silver passes into and alloys with the excess. Silver ores and precipitates are also smelted with lead ores or litharge in water-jacketed furnaces. A highly argentiferous lead is also obtained by the treatment of the zinc crusts removed in Parkes' process for desilverising lead (p. 255).

Cupellation of Rich Lead.—The lead is separated from the silver and gold by exposing the surface of the molten metal at a red heat to the action of a blast of air. The lead combines with oxygen, forming litharge (PbO), which melts, and is blown off the top, thus exposing fresh surfaces to the action of the air. Copper and other

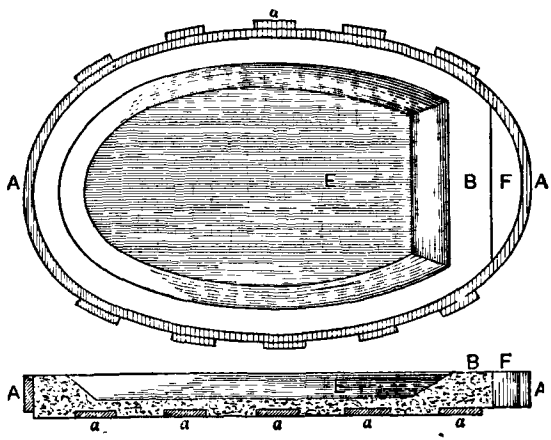


FIG. 144.

base metals present are also oxidised, and the oxides dissolved in the melted lead oxide are carried away by it (see p. 238). The silver and gold, which are unoxidisable, are left behind. Some little is, however, carried away in the oxide, particularly when the alloy becomes very rich. Bismuth remains until the last. In the English cupellation furnace, this oxidation is conducted on a bone-ash cupel, and some of the litharge is absorbed by the porous material. The bed of the German cupellation furnace is made of marl brasque—a mixture of marl, or clay and lime, with wood ashes.

The English cupel or test is made by ramming bone-ash, moistened with a solution of pearl-ash, into an iron frame, with mallets. Cement and other porous basic materials have largely replaced bone-ash. The frame, A, is elliptical in shape, 4 to 5 feet long and 2 feet 6 inches to 3 feet wide, made of 5-inch flat iron, from $\frac{1}{2}$ to $\frac{3}{4}$ inch thick. Five iron ribs, 3 to 4 inches wide and $\frac{1}{2}$ inch thick, cross the bottom (*a*, Fig. 144). The bone-ash is rammed in in layers, and a cavity, E, scooped out with a trowel, leaving the sides about 2 inches thick

round the top and 3 at the bottom, and the bottom itself about 1½ inches thick. At one end, some 5 inches of bone-ash are left, and an opening, F, is made clean through the bottom, leaving a 2-inch dam, B. The litharge is thus prevented from coming into contact with the ironwork and corroding it. The cupel holds about 5 cwts. of lead.

This cupel forms the hearth of the cupellation furnace (Fig. 145). G is the fireplace, C the hearth, and B the stack. A tuyère, N, having a downward direction, enters at the back, and over the door is a hood H, to carry away the fumes of litharge PbO. P is a pot in which the lead is melted. Coal is used as fuel.

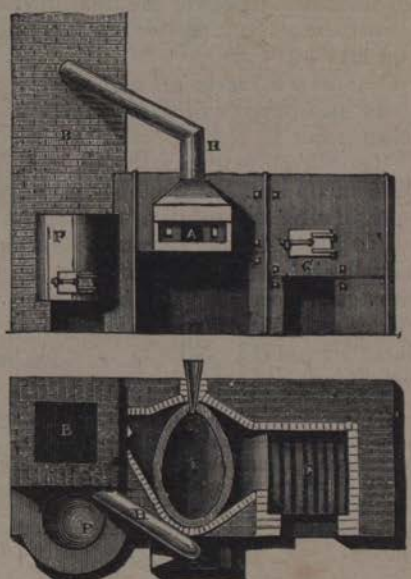


FIG. 145.

The cupel, carefully dried for some days, is placed on a truck, run under the furnace, and lifted into its place, in which it fits loosely. It is secured by wedges, crossbars, or by projecting eyes, and the edge of the iron ring covered with bone-ash. After carefully heating to redness, lead is introduced from the lead-pot, or in pigs, through a channel at the back. The blast is supplied by a fan, or occasionally by a steam jet. The litharge which forms is removed by making a little gutter in the bridge in front, through which it flows into conical iron moulds on wheels, placed beneath to receive it. The furnace is maintained at a cherry-red heat. As the lead is removed by oxidation, fresh additions are made to keep up the level in the cupel.

In working on Pattinson lead containing from 500 to 700 ozs. to the ton, the operation is conducted in two stages. In the initial stage a lead containing 8 per cent.—4,000 to 5,000 ozs. per ton—is produced. The litharge produced in this stage is poor enough in silver to be sent into the market. It is sold for glass-making, etc. The enriched lead is then generally removed, being run into pigs by boring a hole through the bottom of the cupel. More poor lead is then treated in the same cupel after stopping the hole.

The rich lead is then similarly treated on a new test, the litharge being saved separately. It is reduced as described (p. 250), and yields lead containing some 40 ozs. of silver per ton. As the cupellation approaches completion the surface of the metal becomes iridescent

(rainbow tinted) and strikingly beautiful. As the last film of oxide clears off, the metal flashes out brightly, presenting a clear, brilliant, bluish-white appearance, the surface reflecting the roof of the furnace This is known as the " brightening " or " coruscation." The cooling of the silver must be effected slowly to prevent loss by " spitting." This, as already indicated, is prevented by a small amount of impurity, and its occurrence is an index of the purity of the metal. Many curious and fantastic forms result by the throwing up of the surface, partly caused by the escape of oxygen and partly by contraction of the mass expelling the fluid interior. Instead of solidifying in the cupel the silver may be run into moulds by making a hole through the test.

Oil-fired furnaces are also used.

In an ordinary furnace from 4 to 5 cwts. of lead are oxidised per hour, some 1½ cwt. of coal being required.

The silver is generally about 995 to 998 fine. The cupels are broken up and the parts saturated with litharge smelted with fluor-spar in a blast furnace to recover the lead.

Refining.—The refining of impure silver is effected either by cupellation, or, if very impure, such as is sometimes obtained by amalgamation methods, by melting it and exposing it to the air or under oxidising fluxes in crucibles. Copper iron, etc., may thus be largely removed as dross. The purified metal is then refined on bone-ash cupels.

Separation of Silver from Copper.—Formerly a method of separating silver from argentiferous copper by means of lead was largely practised. The copper, melted with about four times its weight of lead, was cast into flat cakes 18 inches in diameter and 3 inches thick. These were then carefully heated and the lead allowed to liquate out, carrying the silver with it. The residues were subjected to a second liquation at a higher temperature. The argentiferous lead was afterwards cupelled.

Treatment of Slimes from Electro-refining Copper (p. 232).—After roasting for 1½ to 8 hours at 700° F. to oxidise copper and other base metals the mud is boiled for several hours with from 15 to 20 per cent. sulphuric acid till silver shows on test in the solution. Sufficient *raw* slimes are added to precipitate any silver dissolved and the liquor syphoned off.

The residue is thoroughly washed finally on an Oliver filter. (If on testing selenium or tellurium is found in the liquor it is boiled with copper foil to precipitate it before sending it back to the tank room.)

The treated slime contains less than 2 per cent. of copper and is furnace refined.

Refining silver slimes containing selenium and tellurium.—The treated slimes containing less than 2 per cent. copper and 25 to 50 per cent. moisture are melted in a magnesite lined reverberatory furnace, some 8 to 10 tons of wet slimes being introduced during 20 hours. During melting lead and much antimony oxidise, and combining with silica produce a glassy slag, which is skimmed off when

completely melted. Air pipes are introduced and the charge thoroughly rabbled for some 6 hours. The remainder of the antimony, the arsenic and some selenium and tellurium are thus removed. Sodium carbonate is added to the charge in considerable amounts and soda nitrate to oxidise selenium, tellurium and copper and remove them with other base metals as a water soluble slag. This is continued till the impurities are eliminated and bullion of 99·5 per cent. purity is obtained. It may contain 98 per cent. silver and 1·5 per cent. gold. This is ladled out and cast into anodes, 6½ by 9 by ½ inches, for electrolytic parting by the Moebius process (p. 303).

The dust produced in melting is recovered in dust catchers, scrubbing towers and Cottrell electric precipitators carrying current at 50,000 volts.

After drying, roasting to remove any selenium and arsenic, the residue of lead and antimony oxides is sent to the lead refinery.

The glassy slag produced in melting down is also sent to the lead works. Selenium and tellurium are recovered from the highly caustic solution of selenite and tellurite of soda obtained by leaching the alkaline slag.

Silver Refining Copper Slimes.[1]—At Copper Cliff, Ontario, the typical slimes contain 24 per cent. copper, 20 per cent. nickel, 15 per cent. selenium, and 3·5 per cent. tellurium with silver, gold, also lead and arsenic. Copper and nickel are removed by treating with concentrated sulphuric acid by a sulphatising roast in an oil-fired reverberatory furnace with a cast-iron hearth. Just enough acid to combine with the copper and nickel is used. The temperature is carefully watched and the charge continually rabbled—see p. 233. The roasted slimes are leached in lead-lined tanks with 10 per cent. sulphuric acid followed by water. The liquor is raised nearly to boiling-point and agitated for an hour by steam fan. After settling, the slimes pass to a 40-inch suspended centrifugal with a rubber-covered steel basket, are washed with hot water, and transferred to the furnace room for treatment in the doré furnace.

Any silver, selenium, and tellurium removed in leaching is precipitated by cement copper. The liquor is returned for re-use and the slime produced given the same treatment as raw slimes.

The treatment of the slime in the doré furnace, and subsequently, follows the usual lines (see above).

[1] Bernard, Copper Metallurgy. American Inst. of Min. and Met. Engineers, 1934.

CHAPTER XVI

GOLD

THE fine yellow colour and brilliant appearance of this metal are well known. It is comparatively soft, being only slightly harder than lead when pure and unalloyed with base metals. It is the most malleable and ductile among metals, leaf $\frac{1}{280000}$ of an inch thick being obtained by hammering, and a grain can be drawn into wire 500 feet long. Its tenacity is about 7 tons per square inch. These properties are influenced greatly by minute quantities of impurity, notably lead, bismuth, antimony, and arsenic. Tellurium and selenium are also very injurious. Its alloys with silver and pure copper are harder, but extremely malleable and ductile. It has a melting-point of about 1064° C., and volatilises at very high temperatures, as in an electric furnace. When molten it appears greenish, and if undisturbed as it cools after solidifying, suddenly flashes out bright when at a temperature of about 600°. It contracts considerably on solidifying. Pure gold welds with the greatest ease. Its flowing power is high, and it is an excellent conductor of heat and electricity. Its specific gravity is 19·3.

The metal is unaffected by dry or moist air, and resists the action of acids (save selenic), alkalies, and sulphuretted hydrogen. It is readily attacked by chlorine, and also by iodine and bromine. A mixture of nitric and hydrochloric acids (aqua regia) dissolves gold, because free chlorine is generated. The gas attacks gold most rapidly at the moment of liberation (nascent state) and is less active when diluted with air or any inert gas. The chloride ($AuCl_3$) is very soluble in water. It is decomposed at high temperatures, gold and chlorine resulting. Gold is slowly dissolved by cyanide of potassium in presence of air or oxygen.

$$2Au + 4KCN + H_2O + O = 2AuCN.KCN + 2KHO$$

The addition of a little bromine or cyanogen bromide hastens the solution. It is precipitated from its solution as chloride by most metals, and also by sulphate of iron, chloride of antimony, oxalic acid, carbon, and carbonaceous bodies. The solution of gold in potassium cyanide is not precipitated by ferrous sulphate or ordinary reducing agents. Metals, as, for example, zinc, throw it down readily. Mercury readily amalgamates gold.

Occurrence.—Gold occurs naturally in the free state, but to some extent also as telluride, and possibly as sulphide. It is intimately associated with iron pyrites and other sulphides, the greater part of the gold in some ores being contained in the pyritical contents. Native gold occurs in matrix, generally in veins of quartzose and other

hard rocks, forming reefs or dykes, and in deposits formed of the debris produced by the weathering of such rocks, such as "alluvium," river sand, etc. In the latter formations, owing to the action of running water, the lightest portions have been transported furthest, and, owing to the high specific gravity of the metal, an accumulation of the coarser gold has taken place nearest to the broken-down rock. Alluvial deposits are, in consequence, often richer than the mother rock from which they are derived. The gold occurs in all degrees of coarseness, from microscopic particles to masses of considerable size. These are known as "nuggets." The "Maitland Bar" nugget from New South Wales, exhibited at the Mining Exhibition of 1890, contained 313·093 ozs. of fine gold. Others much larger, such as the "Welcome Stranger" and "Precious," have been found. Gold is very widely distributed in small quantities.

In Great Britain, it has been found in Cornwall, Wales, Perthshire, and Sutherlandshire; in Ireland, in Wicklow; and in the Isle of Man.

In Europe, Hungary, Transylvania, Sweden, Spain, and Italy also furnish gold.

Rich deposits occur in India, Ceylon, China, Japan, Siberia, the Ural Mountains, and in South Africa.

In the New World, the gold-bearing rocks occupy the west coast, following the line of the mountains. Alaska, British Columbia, California, Mexico, Bolivia, Peru, Chili, Colombia, and Brazil are all rich in gold. South Africa and Australia are at present the principal gold-producing countries.

The high value of the metal enables deposits which contain very little gold—in some cases only a few grains per ton—to be profitably worked. Much depends on the nature of the deposit and the method adopted.

Alluvial Deposits, Placers, etc.—The mining and extraction of gold are almost inseparable. Alluvial deposits differ very much in character, from loose sand, pebbles, etc., through stiff earth, to hard conglomerate, the pebbles of which are firmly cemented together. The "banket ore" of South Africa is of this class, although many of the pieces are angular.

The gold in alluvium occurs in nuggets of varying size, and in grains. In surface deposits (placers), generally shallow, the ground is first picked over for nuggets. The sand and gravel are then washed, the lighter materials being thus removed, and gold remains.[1]

Panning out consists of washing the "pay-dirt" in a shallow iron pan with a depression in the middle for retaining the gold. The earth is placed in the pan and washed under water, a circular motion being given to it. Light matters are carried over the edge, and the gold gradually finds its way to the bottom, together with other heavy matters. This residue is dried, and the lighter materials blown away, leaving the gold. In Africa the natives wash the river sand in gourds, mixing it up with water and pouring off the matter held in suspension. They store the gold dust obtained in quills.

[1] "Drag line" dredges are being installed in loose "placer" mining.

Hydraulic Mining.—In this method of working, the auriferous gravel is dislodged by means of a powerful jet of water directed against the bank by means of an iron nozzle (monitor). The quantity of water required for this purpose is enormous. It is sometimes carried for miles down hillsides and across valleys, in pipes on trestles (flumes), and is delivered at high pressures, sometimes under a head of 500 feet. The dislodged material is carried by the stream of water down a series of long wooden troughs—the "sluice"—made in 12-feet lengths, fitted together, which have a slope of about an inch to the foot, more or less. The bottoms of these are crossed at intervals by movable wooden or iron bars, *riffles*, behind which the heavy particles of gold, which move more slowly and have a greater tendency to settle, lodge. The lighter gravel, etc., is carried on by the current. Perforated iron plates, *grizzlys*, are introduced at intervals in the bottom of the sluices. The coarse gravel is carried on over these, but the finer portions fall through the plate on to a second sluice at a lower level, with a separate water supply. The inclination of this is less than the first, and the lower velocity of the stream favours the collection of the fine particles.

Mercury is fed in small quantities from time to time at the top of the sluice. It lodges behind the riffles and catches the particles of gold which come in contact with it. Amalgamated copper plates are often suspended in the sluice to catch the "float gold" (very small flattened particles which float on the surface).

The amalgam is removed at intervals. For this purpose the water is stopped, the gravel cleaned out and the riffle bars lifted in order, commencing at the top, and the amalgam collected. The upper part of the sluice is cleaned up at frequent intervals, the greater part of the gold being caught there. After squeezing out the excess of mercury through chamois leather, the amalgam is retorted.

Washing Sands, etc.—Baize, blankets, and hides, with the hairy side up, are sometimes employed in the washing of fine sands and stamped material. They are attached to sloping boards which form the bottom of shallow sluices. The sand is thrown on at the top, washed down by a stream of water, and brushed by a workman against the stream. From time to time the blankets, etc., are removed, and the gold, etc., shaken out into a trough of water and amalgamated with mercury. The amalgam is afterwards retorted.

A very effective method of treating fine sands is to boil them with water and mercury. Chinamen find it profitable to work over the "panned-out placers" in California in this way.

Hard "cements" (consolidated alluvium) are often ground in mills resembling mortar-mills, the "pulp" or ground material being carried away over amalgamated copper plates.

Treatment of Gold Quartz.—Much depends on the mode of occurrence of the gold and the nature of the quartz. In some ores gold occurs entirely in the free state, and free from pyrites. Such ores are often ferruginous, the oxide of iron resulting from the decom-

position of iron pyrites. The gold often exists in largest quantity in the oxide of iron, showing it to have been derived from the pyrites. Such ores generally become pyritous below the water-line. "Gossans" consist mainly of this decomposed pyritous material.

In quartz containing pyrites, much of the gold is often contained in the pyrites. Most of this escapes extraction by the ordinary amalgamation processes, either owing to its extreme state of division, or to combination as sulphide in the pyrites. It passes into the "tailings," as the residues from amalgamation are called. Such ores are described as "refractory," and require special treatment. Ores in which all the gold is recovered by simple crushing and amalgamation are described as "free milling."

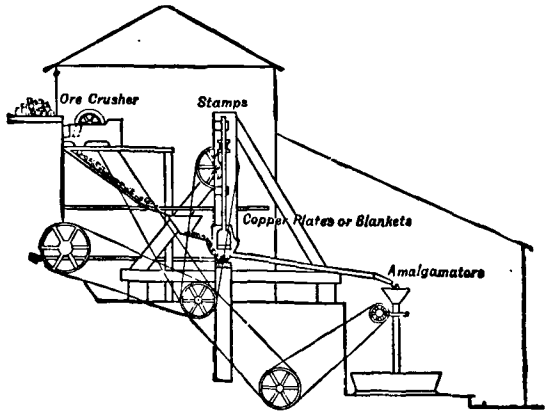


FIG. 146.—Wet-crushing gold-mill.

The loss of gold in the tailings may be due to—

(1) The fine state of division.
(2) Presence in sulphides, arsenides, tellurides.
(3) Fouling of the mercury surface:
  (*a*) by contact with impurities in the ore, such as sulphantimonides and sulpharsenides;
  (*b*) by oxidation of the copper or other base metal in the mercury, whether present originally, taken up from the plate in the early stages of use of the plate, or deposited from solution. Such metals as copper, lead, and bismuth may occur native or as compounds decomposed by mercury. Fragments of brass and copper, and even white metal bearings may find their way into the mortar box and are taken up by the mercury, and occasion great loss.

Amalgamation of Free-milling Ores.—The quartz is first broken into about inch cubes in a stone-breaker or ore crusher (Fig. 146), the jaws being so adjusted as to deliver it of the required size.

The ore is next crushed to fine powder under stamps, or by rolls, or grinding mills.

Fig. 147 shows a stamp battery. The stamps consist of heavy cast-iron "heads," or "bosses," A, shod with steel, attached to long wrought-iron or steel stems sliding in hardwood "guides" BB. These are lifted by the "cams" C, attached to the revolving "cam shaft" D, driven by the pulley E, acting on the "tappets" F, keyed on the stems. The cams are right- and left-handed, so that each head is raised twice at each revolution. Under each stamp is a steel-faced "die" G, between which and the falling head the ore is crushed.

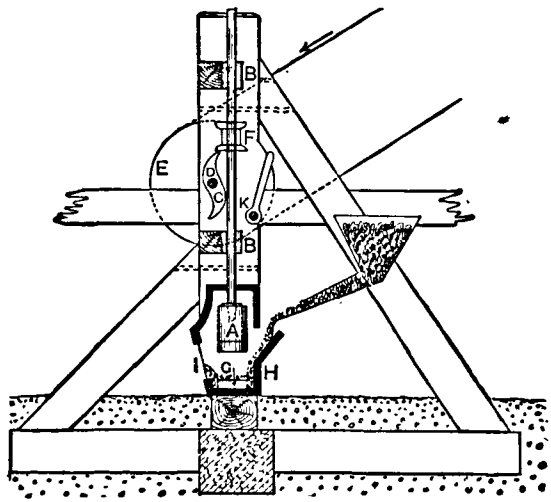


FIG. 147.

The dies are contained in the cast-iron "mortar box" H, which is supported on a wooden foundation on pads of indiarubber a quarter of an inch thick. One or both sides of the mortar is fitted with "screens" I, of perforated sheet iron or thick wire cloth, and a stream of water is fed in from a pipe. Some 72 gallons per hour per head is required, but it may be recovered in settlers with a loss of about 25 per cent. The ore is fed in on the side opposite the screens (if single discharge), often by an automatic contrivance. The action of the cams on the tappets not only raises the head, but turns it partially round each stroke, and thus causes it and the die to wear uniformly. For gold crushing, the mortar-box is lined with amalgamated copper plates, and much of the coarse gold is caught in the mortar. A little mercury—half a thimbleful—is fed in at intervals for this purpose. Levers on "jack" shafts, K, are provided for holding up the stamps when necessary.

The heads, with attachments, weigh from 4 to 10 cwts., but for quartz, generally about 7 cwts.

They have a drop of about 10 to 12 inches, and give from 70 to 80 blows per minute, the cam shaft making from 35 to 40 revolutions per minute. The fall of the head splashes the pulp against the screen and assists in forcing it through. The screens have a mesh of from 30 to 60 per linear inch. Each head will crush 2 to 2½ tons per day (wet crushing).

The fine material, "pulp," is carried by the water through the screens, on to amalgamated copper plates (Fig. 148), slightly inclined, over which it is carried by the current, the free gold dragging along the bottom and being arrested by the mercury.

The plate next the mortar is sometimes silver-plated, to prevent the deadening of the mercury by oxidation of the copper dissolved in it, making it much less active.

From the plates the "tailings" may pass to amalgamators or to vanners, as subsequently described.

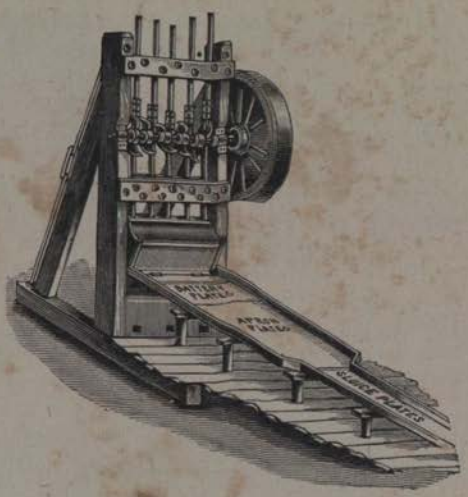


FIG. 148.—Stamp battery.

Gold tailings (1) may be mechanically concentrated on vanners or other appliances to separate auriferous sulphides and other heavy matters, which are subsequently treated.

(2) May be cyanided direct (if not slimy) in vats. If slimy, must be washed to separate slimes before putting into vats.

(3) Slimes if sufficiently rich may be cyanided in agitators and filter pressed to recover the gold liquor before precipitation with zinc.

Stamp batteries, "dry" or "wet," are open to several objections. The principal one is the tendency to cut up and flatten out coarse particles of gold. By the repeated hammering a hard surface is developed, and fine particles of foreign matters driven into the soft metal. This renders it very difficult to amalgamate, the mercury only attacking it with extreme slowness. There is also liability to loss from the production of "float gold."

Rolls are open to fewer objections, cracking open the ore and exposing the metal. Fig. 149 shows the Huntingdon Mill. The pan is of cast iron with a steel belt round the lower part inside. Rollers are supported vertically on rods, on which they revolve by friction against the side of the pan. The head from which they are carried is revolved at 70 revolutions per minute. The mullers are pressed by centrifugal force against the ring, and the ore coming between is crushed. Above the steel roller path is a screen occupying half the circumference of the pan. A stream of water is fed in above, and stirrers are provided to ensure complete crushing. For soft ores a mill having a 5-foot pan is about equal to a 10-head stamp battery, and requires only about half the power to drive it.

Ball mills are now largely employed for fine grinding.

Tube Mills.—More modern practice has tended to use the stamp mill for comparatively coarse crushing, by using coarser screens and setting them lower in order to obtain more rapid delivery. Less gold is recovered in the mortar box and on the battery plates. The sand is classified and the coarse portion reground in pans or tube mills. (Fig. 150.)

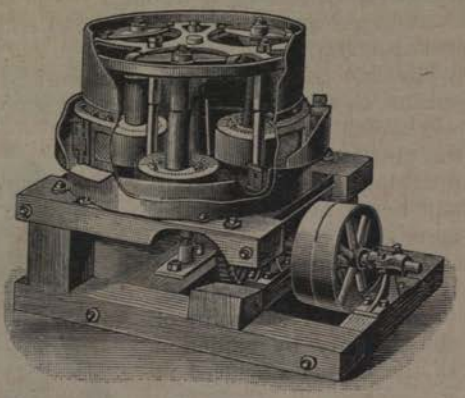
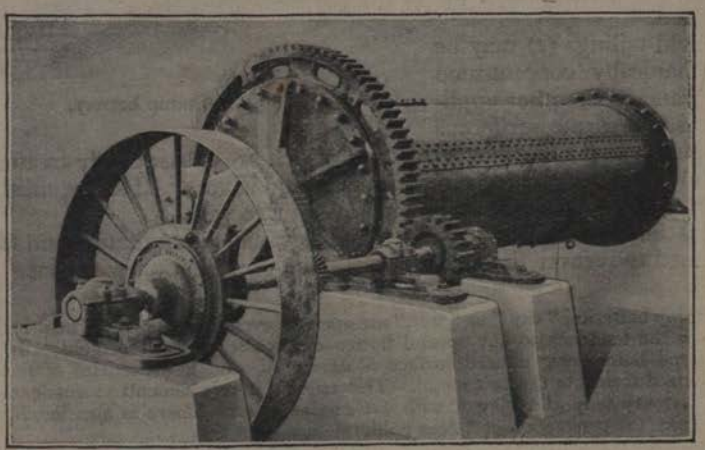


FIG. 149.

The latter consist of a tubular steel body or drum made of half-inch steel plates, lined with plates of hard cast iron or with flint slabs set in cement.[1] The ends are of cast steel. The drum is from 12 to 16 feet long and 3 to 6 feet internal diameter. It is supported on hollow trunnions, on which it revolves ; through one of these it is fed. The discharge is effected at the other end through a grating, which



Sandycroft Foundry Co., Chester.]

FIG. 150.—Tube mill.

closes the end of the chamber, and thence to the hollow trunnion. The chamber is half filled with flint balls, varying in diameter from 3 to 4 inches to 1 inch, and makes from 20 to 35 revolutions per minute.

[1] Recently *linings* of rubber have been successfully applied.

Chilled iron and manganese steel balls are also used. The chamber is lined with the same material as the balls. In passing through the mill the ore is very finely ground. Tube mills operate on both dry material and on wet pulp from which the bulk of the water has been removed. Thick pulp gives the best grinding. Mercury is sometimes fed into the mill. The product of the mill is mixed with water and passed over amalgamated shaking-plates to collect the gold and amalgam.

Cleaning up.—The mill is stopped periodically for the purpose of collecting the amalgam, which is carefully removed from the amalgamated plates. It is worked up with fresh mercury either by hand or in pans (clean-up pans), and well washed with water to remove earthy and other matters. It is then squeezed in bags of canvas or chamois leather to expel the excess of mercury. This is not free from gold, but is re-used. The pasty amalgam remaining in the bag is retorted to remove the mercury. The gold which remains is melted in crucibles and refined.

Loss of Mercury.—This arises from two causes, "sickening" and "flouring." In the former case, the mercury is converted into a black powder and carried away. It is caused by the presence in the ore of certain minerals, *e.g.* antimony sulphide.

Sodium amalgam is added to keep the mercury clean and active.

"Flouring" is breaking up of the mercury into minute globules, which are lost.

Treatment of Tailings in Amalgamators.—Formerly the tailings were passed into amalgamators, in which they were ground up with mercury. In modern practice they are treated by the cyanide process.

In the amalgamator shown in Fig. 151 the pulp is fed into the hopper A, and passes down the hollow shaft B, to which is attached the iron muller C. This is slowly rotated; the outer pan D contains mercury, below which the muller dips.

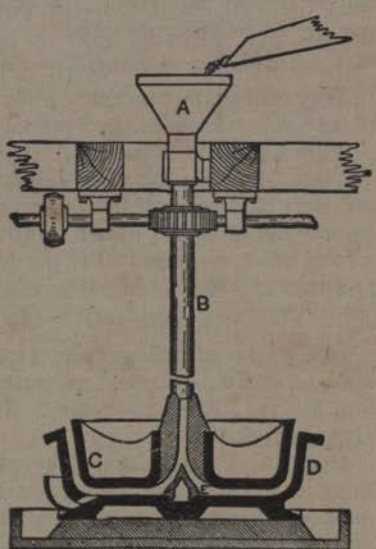


FIG. 151.—Continuous amalgamating pan.

The pulp is delivered, by the openings E, *under the muller*, which, by its revolution, thoroughly incorporates the tailings with the mercury. They escape over the edge of the pan, and may be delivered to a second set of amalgamators at a lower level, or pass direct to settlers.

The Hungarian mill for the amalgamation of iron pyrites is in principle exactly similar, but is driven from below. Amalgamators of other types were also employed.

The tailings were more commonly treated on Frue vanners or other contrivances for the recovery of the heavy sulphides—iron pyrites, galena, copper pyrites, etc.—which they contained, and which often carried a considerable portion of the gold present in the ore. This is not recovered by simple crushing. The "concentrates," as they are termed, were either ground in iron pans with mercury, as in the treatment of silver ores, or otherwise dealt with. In most cases the whole of the pulp is treated *without concentration* with a solution of potassium cyanide (see below).

Pyritical materials and concentrates were formerly treated by **chlorination methods** for the recovery of the gold. The pyritical matters were calcined and after moistening were placed in suitable vats or other receptacles and subjected to the action of chlorine gas, or they were mixed with bleaching powder or other materials yielding chlorine. In this way the gold was converted into gold chloride while the oxide of iron was not attacked. The chloride was dissolved out in water and the gold precipitated by ferrous sulphate (copperas) or other material

$$6FeSO_4 + 2AuCl_3 = 2Fe_2(SO_4)_3 + Fe_2Cl_6 + 2Au$$

Very elaborate processes were evolved, but they have been completely superseded by the cyanide process.

The Cyanide Process, introduced by Messrs. MacArthur and Forrest, depends on the well-known fact that potassium cyanide attacks gold in the presence of oxygen, and if in a fine state of division, rapidly dissolves it. Weak solutions are found to be more active than strong ones, on account of the greater solubility of oxygen in them (*Journal of Chemical Society*, 1893).

$$4KCN + 2Au + O + H_2O = 2KCN.AuCN + 2KHO$$

One great advantage possessed by this process is that raw pulp may be treated directly, no concentration by washing on vanners or buddles, etc., being necessary. In the case of most ores calcining is also unnecessary.

General Principles.—The general outline of the process is the same in all cases, but the particular procedure adopted varies with the method of occurrence of the gold, the nature of the rock matrix and the gold-bearing mineral. The ground material is left in contact with the solution for a period varying from 60 to 72 hours with continuous circulation or agitation, the clear solution being afterwards brought into contact with zinc shavings or zinc powder to precipitate the gold, or passed through electrolytic cells to deposit the gold. The spent liquors in each case are returned to the storage tanks for re-use.

Generally the whole of the material can be treated directly. In some cases, *e.g.* in the presence of graphite and other carbonaceous

matters, and some other minerals that precipitate gold, it may be necessary to concentrate or calcine to eliminate the interfering bodies and open up the ore for extraction.

The gold is precipitated by the zinc as a black powder. It is collected periodically, washed to free it from zinc as far as possible, and melted with fluxes in crucibles. A very coarse bullion is obtained, and slag. About 90 per cent. of the gold is obtained, and the liquors may be re-used. The foreign matters in the ores are not attacked.

Refractory ores which cannot be successfully treated in any other direct way may be thus dealt with. The process is in almost universal use throughout the world. It is not applicable to coarse gold, and is used for tailings and concentrates only. The danger arising from the use of such a powerful poison as cyanide is very small, if cleanliness and perfect ventilation are attended to.

In the Siemens-Halske process the gold is precipitated by electro-deposition.

Sulman adds cyanogen bromide to the ordinary solution, which greatly reduces the time, and is more effective. The precipitation is effected by zinc fume instead of shavings (see p. 323).

Tailings containing much pyrites (especially copper) are difficult to treat. On exposure to the atmosphere in the moist state they oxidise. Free acid and soluble salts are formed, which greatly increase the consumption of cyanide. Lime is used to neutralise the ore and decompose soluble sulphates.

Rich slimes are agitated with the solution and filtered through a filter press.

The efficiency of the extraction depends on the perfection of contact with the solvent.

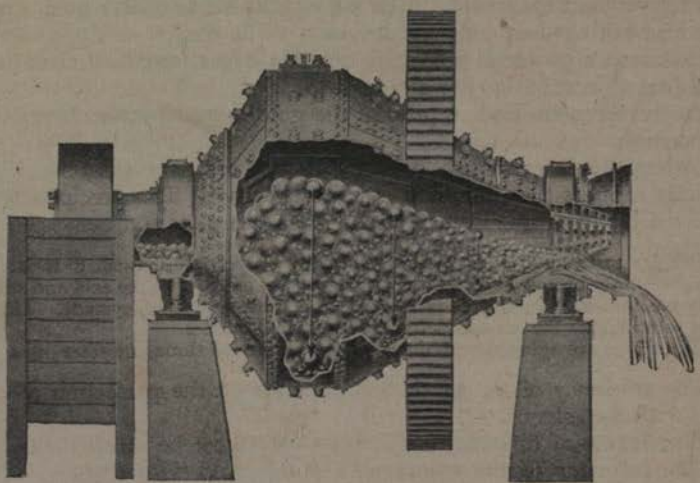
The degree of fineness to which the ore must be crushed depends on the intimacy of the association of the gold with the ore. It is necessary to expose the gold to the action of the solution. Hence for tailings and general ores the finer the grinding the more perfect the all through extraction. On this account tube and ball mills of improved types are employed. The Hardinge mill is shown in Fig. 152. Owing to the shape of the chamber the larger balls are retained in the wider end. The fineness of the particles greatly influences the method of treatment with the solution. Coarse particles settle readily and afford ready passage for the solution. They also permit of the whole pulp being wetted and so promote free circulation and uniform extraction of the gold. They are "sandy" in character. The liquors from the treatment tanks are clear and do not require filtering. In cases where comparatively coarse crushing suffices the ore can be treated at a minimum of cost.

Fine particles, on the other hand, settle badly, and the circulation is very slow and irregular, so that the operation is prolonged and the extraction by percolation processes poor. When wetted they form "slimes."

Ores vary greatly in their behaviour on crushing. Some ores are of uniform hardness and character, and break down into particles of uniform size. Others consist of hard and soft portions and sometimes

of different materials which behave differently on crushing, so that by the time the hard materials are fine enough the others are in very fine particles and form slimes. In such cases, owing to the interference with the circulation caused by the presence of the fine particles, it is necessary to separate them to secure complete extraction.

The "sands"[1] and "slimes"[2] are examined separately to ascertain whether the gold occurs in the material that produces the slimes or in the harder material producing sands. If one is "barren" it is thrown away after separation, or if some gold be present it may be subjected to special treatment.



Fraser & Chalmers, Ltd., Erith.]

FIG. 152.—Hardinge mill.

In some cases to secure satisfactory extraction it is necessary to reduce the whole material to the condition of slime and subject it to special treatment. "All sliming" processes must be followed in the treatment of telluric, antimonial, and other refractory ores.

In dealing with ores containing coarse gold the ores are first amalgamated and the tailings are, after settling, and if necessary other treatment, cyanided.

The slimes, whether separated from sands or produced by fine grinding all the ore, are treated with cyanide solution in agitator tanks provided with mechanical stirring arrangements, and air and steam jets for aeration and heating if deemed necessary. Agitation is necessary to bring the material and solvent into contact; aeration both agitates and assists in the reaction.

Refractory ores are most readily attacked by hot solution.

[1] Material passing 40–60 mesh.

[2] Material ground to pass 200 mesh; most of it will pass 300 mesh.

The Cyanide Solution.—Solutions varying in strength from 0·1 to 0·5 per cent. are employed according to results of preliminary tests made with a view to securing a full yield with minimum cyanide consumption. Large volumes of weak solution may be more effective than smaller bulk of stronger solution.

Sodium cyanide (NaCN) is used containing 85 per cent. of the cyanide, but is always quoted in terms of potassium cyanide KCN. Thus an 85 per cent. sodium cyanide (NaCN) becomes 106 per cent. KCN. The remainder consists of carbonate and other impurities.

A solution is made up to a fixed strength and used for bringing the spent liquor from the precipitating boxes and wash waters up to the normal working strength.

The treatment of sands is carried out in large tanks, often of very large size, constructed of wood, iron, or concrete, provided with false bottoms so constructed that free access is given underneath the ore load for leaching liquor and drainage.

The greatest possible care is taken to lay the material evenly in the tanks, and special devices for distributing the sand are employed.

The Dorr distributing machine delivers the pulp, in suspension in water, by means of hollow revolving arms from which the pulp is delivered in a series of jets, which cause the arms to revolve by reaction. In this way water packing is secured, and free circulation of the liquors. The first additions of solvent are admitted under the false bottom so as to rise upward through the material carrying the air before it and preventing the formation of air pockets which would isolate portions of the charge and prevent solution of the gold.

These tanks are provided with appliances both for circulating and uniformly distributing cyanide solution or wash water—over the top of the tank. Provision is made often for *mechanically* distributing the material and for discharging after treatment. In some cases loading is done by hand, the charge being wheeled or dumped in and raked level with care.

Solution—about ½ ton per ton of ore—is admitted under the charge and allowed to rise to the top, after which any further additions are made from the top, the circulation pumps set going, and maintained for from 60 to 72 hours. When extraction is complete the solution is drawn off and sent to the precipitating boxes.

After the first leach the ore is washed with weak cyanide—spent liquor from the zinc boxes—and washed before emptying. This may be done by hand shovelling or through side or bottom doors, or by crane excavators. In suitable situations the tailings may be sluiced away.

Careful supervision is kept on the consumption of cyanide and extraction by assaying both residues and solutions.

Treatment of Slimes.—Slimes where purposely produced by fine grinding the ore in an "all sliming" plant dealing with refractory ores or only those portions produced in ordinary grinding with soft ores, often clayey, or ferruginous, are first settled and dewatered.

In exceptional cases they may be treated by flotation processes (see p. 38) to concentrate rich material. Ores in which much pyrite occurs, arsenical, antimonial and telluric ores and those containing graphite and carbonaceous matter are often calcined prior to treatment. This should be done at a sufficiently high temperature to decompose sulphates formed during roasting as these destroy cyanide—act as cyanicides—and prevent solution. Special reverberatory and multiple-decker furnaces are employed.

The slimes, if wet, are settled and dewatered by vacuum suction filtration to a maximum of 20 to 25 per cent. water in order to avoid diluting the cyanide solution too much. They are treated in Dorr or other agitating tanks of up to 80 tons ore capacity and 160 tons solution. Agitators, both mechanical and air jet, are provided, and the agitation continued for 48 to 60 hours. The solution is filtered through vacuum continuous filters (Oliver, Butters and other types being employed), the pulp washed, and finally the solution is clarified in filter presses before being sent to the zinc precipitating boxes. The strength of the solution varies from 0·1 to 0·5 per cent. cyanide.

Refractory Ores and Concentrates.—These may be treated directly or undergo a preliminary calcination. The latter method yields the better extraction. In one case an ore yielding 80 per cent. by direct treatment yielded 95 per cent. of its gold after calcining. Telluric, antimonial, and arsenical ores are all rendered easier of extraction by calcining. In any case, the ore is ground to a " slime " and agitated with the cyanide solution, either in the cold or with the aid of heat—if available and the ore is sufficiently rich. The extraction is better and more quickly effected. Cyanogen bromide is sometimes added to the ordinary solution. It reduces the time and is more effective. Ores and tailings containing a few dwts. of gold per ton can be economically treated.

Loss of Cyanide.—Tailings and ores containing much pyrites (especially copper pyrites) and other oxidisable minerals are difficult to treat. The soluble salts formed on exposure in the moist state decompose the cyanide and increase the amount required. Careful tests are made to determine the consumption and the best strengths of solution for any given ore. Lime is used to neutralise the ore and decompose the sulphates. It is only partially effective. In many cases washing is much more satisfactory if water is available and it can be done.

Recovery of the Gold.—The gold is precipitated from the solution—

(1) By passing it through boxes containing metallic zinc in fine shavings. The gold is easily precipitated and remains as a purplish-black powder in the boxes.

(2) By agitating the solution with zinc powder and filtering off the precipitated gold in a filter press.

(3) By electrolytic methods.

The first method is generally employed. The reaction is

$$2AuCNNaCN + Zn = Zn(CN)_2 2NaCN + 2Au$$

Fig. 153 shows the zinc boxes.

The zinc box consists of several compartments, usually six, each of which has a partition extending nearly to the bottom. The solution is fed in at one end, " the head box," and passes slowly through each compartment in succession, the overflow from each being conducted to the bottom of the next. Each compartment contains a basket or loose perforated sheet metal container filled with very fine zinc shavings which provide a large surface and ensure rapid and complete precipitation.

The metals precipitated from alkaline cyanide solutions by zinc are gold, silver, copper, antimony, arsenic, mercury, lead, and occasionally nickel, cobalt, and cadmium. Selenium and tellurium may also be present. Gold is among the first metals precipitated by

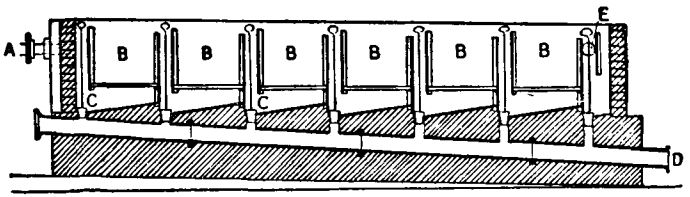


FIG. 153.—Zinc boxes for precipitating gold from cyanide solution. A, liquor inlet; B, chambers containing zinc shavings; C, plugs for withdrawing sludge; D, clean-up pipe; E, outlet for spent solution.

zinc, most of the silver is precipitated later. In addition sulphate and carbonate of lime, ferrocyanides, and silica accumulate in the zinc boxes.

To render the zinc more active small continuous additions of lead acetate solution are sometimes made at the head box.

Precipitation of the gold only proceeds freely in the presence of free cyanide. If the solution contains none it must be added as the solution enters the box. It should be alkaline. At first the precipitate adheres to the zinc, but afterwards falls and constitutes the mud of a purplish-black colour.

ANALYSES OF SLIMES FROM ZINC BOX AT KARANGAHAKE.[1]

	A.	B.	C.	D.	E.	F.
Gold	1·72	3·13	3·76	0·98	0·14	0·16
Silver	23·80	32·14	37·51	28·74	16·78	19·20
Copper	2·64	4·08	3·68	8·24	12·00	4·88
Iron	—	2·28	13·86	6·02	10·13	—
Nickel and cobalt	1·26	2·07	trace	—	—	—
Manganese	—	1·85	2·86	—	—	—
Zinc	26.00	41·65	29·88	40·93	44·78	[2]
Insoluble matter	40·00	4·44	3·20	7·20	7·83	5·58

[1] " Gold Refining," D. Clark, p. 74.

[2] Not estimated.

After washing through fine gauze to separate most of the zinc the slimes when air dried contained about 40 per cent. bullion, gold and silver being in the ratio of about 1 : 20.

Such slimes may be treated in several ways. They may be roasted on iron trays to burn off any organic matter and to oxidise the base metals present more or less completely. Afterwards they are mixed with borax, soda, fluorspar, and sometimes sand and oxidising fluxes and melted in plumbago crucibles. Bullion of a fineness of 950 may be obtained in this way, but the losses as dust and in the slag may be heavy.

In most cases the slimes receive a preliminary treatment with sulphuric acid to remove the free zinc. The gases evolved usually contain arsenical, antimonial, telluric, and selenic compounds, which are both objectionable and dangerous, and closed or hooded vats must be employed for this purpose. In addition, hydrocyanic acid is present in small quantity.

The sludge is filtered through a " frame," preferably a 3-frame filter press, to ensure the retention of the fine gold, and after washing dried in shallow cast-iron trays and afterwards heated to redness in a muffle for some hours. It is afterwards smelted in crucibles or in special tilting furnaces.

Bullion from cyanide plants may be largely contaminated by copper, antimony, lead, tellurium, and selenium, and other metals. The amounts of the last two are small when the ores are roasted before cyaniding, and greatest when brom-cyanide solutions are used on raw ores. Smelted in fireclay pots it is possible to use oxidising fluxes, but in plumbago pots this is impossible, and the reducing action of the carbon prevents the removal of the impurities. Such pots are, however, less liable to crack, hence their use. The slag should be a clear glass, otherwise it is very liable to carry gold. With poor ores and poor filtration, which permits a large amount of siliceous matter to pass to the zinc boxes, it may be larger in amount than the bullion.

The pots are carefully skimmed to avoid loss of bullion by a mop of slag on the end of an iron rod.

The presence of sulphides or sulphates in the precipitate is objectionable, as they increase the loss of bullion in smelting.

Electrolytic methods of recovering the gold from cyanide solutions are also in use. In the Siemens-Halske process lead electrodes are in use, the gold being recovered from the lead by cupellation.

Attempts have been successfully made to produce purer gold bullion by removal of the silver during the treatment of slimes. The slimes are treated with sulphuric acid and nitre cake ($NaHSO_4$) in an iron pot gradually raised to dull redness. The fused product is boiled out with water and the residue washed by decantation. Bullion ranging from 900 to 997 fine may be produced. The silver is afterwards recovered from the solution by precipitation with copper or by electrolytic methods.

Treatment by concentration of the precious metals by lead and subsequent cupellation of the reduced lead is also followed. After dissolving out zinc the residues are washed and dried, mixed with litharge, silica, slags, and coal dust, and smelted in a small furnace. Iron is added towards the end of the operation to complete the reduction of the lead. The lead is cupelled in the usual way, the only difference being the addition of a flux consisting of borax, soda-ash and silica made at the end of the operation to produce a slag, which is run off. The gold cake is broken up and melted in crucibles with a little flux.

Parting.—Native gold and gold bullion almost invariably contain silver and other metals. The base metals may be removed by cupellation, or, if fairly pure, by fusion with nitre and borax; but silver, platinum, etc., will remain, and must be removed by chemical means. This process is known as "parting" and consists of dissolving out the silver by acids.

Alloys of even base metals with gold are not attacked unless the base metal is in large excess; and hence, if a sufficient proportion of silver is not present, enough must be added to ensure its being acted on.

Sulphuric Acid Parting.—Silver is soluble in hot, strong sulphuric acid, forming sulphate of silver. The alloy to be parted must contain not less than 60 per cent. of silver; generally the alloys treated contain very much more. The metal is granulated by pouring it into cold water, so as to offer a large surface to the action of the acid.

The parting pans are usually of white cast iron, about 2 feet wide, provided with a lid and a pipe by which the sulphur dioxide SO_2 generated is conveyed into a lead chamber for reconversion into sulphuric acid, to be re-used.

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2$$

The pots are heated by fires from below. The granulated metal is treated with about $2\frac{1}{2}$ times its weight of strong acid, at a temperature about the boiling-point of sulphuric acid. The sulphate of silver which forms separates in a pasty mass of small crystals. This is thrown into water in a lead-lined tank and heated by steam. The sulphate dissolves, and the gold settles out and is washed and collected. It still retains silver, and is next treated with sulphuric acid and sulphate of soda in the proportions of 3 to 5, and strongly heated.

The sulphate raises the boiling-point of the acid, and enables it to attack the remaining silver. A second treatment is sometimes necessary. What remains in the pans is then boiled with acid, and the residue washed, dried, and fused.

The solution of sulphate of silver is decomposed by copper ($Ag_2SO_4 + Cu = CuSO_4 + 2Ag$), and the precipitated silver compressed by hydraulic pressure, dried, melted in crucibles, and cast into ingots. The copper is afterwards deposited by iron; or the

solution is concentrated, and the copper sulphate allowed to crystallise out, and sent into the market, the mother liquor being further concentrated in glass or platinum vessels, to recover the excess acid for re-use.

In Gutzkow's improved process the sulphate of silver crystals are dried and heated with from 4 to 5 per cent. of coke dust or charcoal. The silver sulphate is reduced thus—

$$Ag_2SO_4 + C = 2Ag + CO_2 + SO_2$$

The washings from the crystallised sulphate are treated as before by precipitation with copper.

Silver containing more than three grains of gold per pound can be economically treated by this method.[1] Much old silver plate was sacrificed for the gold contained in it when this process was introduced, the older method of parting by nitric acid being too expensive.

Parting with Nitric Acid.—In this process, nitric acid is substituted for sulphuric acid. The operation is conducted in platinum, glass, or porcelain stills, with covers connected with condensers, to recover the acid which is boiled off. Nitric acid does not readily attack the alloy unless it contains about three times as much silver as gold.[2] If less be present, it is melted with more silver, to make up that amount. This is known as *inquartation*. The alloy is granulated and boiled with about twice its weight of nitric acid, diluted with one-third its bulk of water. Red fumes are evolved as long as silver is dissolving.

$$6Ag + 8HNO_3 = 6AgNO_3 + 4H_2O + 2NO$$

The solution of nitrate of silver is drawn off, and the residual gold treated with a little strong nitric acid, and after washing, melted under borax and cast into ingots.

Double acid parting is sometimes resorted to. The granulated alloy is first treated with nitric acid and after thorough washing the gold treated in cast-iron pots with sulphuric acid and nitre and evaporated almost to dryness, more sulphuric acid added and after heating the solution removed and the gold washed, filtered, dried, and melted. Gold thus treated had a fineness of 998.

The silver is recovered by adding hydrochloric acid to the solution of silver nitrate, which precipitates the silver as chloride.

The acid is added cautiously, so as to leave a little silver unprecipitated in order that the nitric acid formed may be re-used.

$$AgNO_3 + HCl = AgCl + HNO_3$$

If free hydrochloric acid were present in the acid used for parting, the gold also would be attacked by the chlorine generated. It is detected by the addition of silver nitrate to the acid.

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[1] This was true under the old conditions.

[2] The amount actually required is less. Complete removal of the silver may be secured with two and a half times the weight of gold present.

The silver chloride is reduced by zinc (see Reduction of the Iodide, p. 279), or by fusion with sodium carbonate, p. 266.

Separation from Platinum.—In parting with nitric acid, platinum, if present to a less extent than 9 per cent. of the silver, is dissolved out. If much platinum is alloyed with the gold, it is best separated by solution in aqua regia and precipitation of the platinum as $2NH_4Cl.PtCl_4$ by sal-ammoniac.

Alluvial gold often contains grains of a heavy, very hard alloy of osm.-iridium, which is not taken up by the gold when melted. In the American Mint this is separated by melting the metal in tall crucibles, when it sinks owing to its greater specific gravity. Silver is also alloyed with the metal to lower its specific gravity and permit the osm.-iridium to sink more rapidly. The upper layers are ladled out and parted, and a fresh batch treated. The residue at the bottom is re-melted with silver several times to diminish the gold present, and then parted with nitric acid. The silver dissolves and the grains of osm.-iridium remain mixed with a little pulverulent gold, which is separated by washing. The alloy is used for the tips of gold nibs of fountain pens.

Electrolytic Parting.

Electrolytic Separation of Silver.—The tanks employed in the **Thun** process measure 48 by 24 by 7 inches, and may be of chemical stoneware or asphalte-lined concrete. The bottoms are lined with half-inch graphite slabs, which form the cathode surfaces.

A strong wooden frame with slats across the bottom for supporting the anodes rests horizontally on the top of one end of the tank. It occupies about half the length of the tank and is partly immersed in the electrolyte.

The other half of the tank is left open and uncovered.

The anodes are enclosed in a slight wooden frame lined with muslin and covered with a close-fitting canvas bag. This frame is placed flatwise on the slats of the tank frame.

The contacts are made by silver plates—candlesticks—resting on the anode and graphite slabs. The silver as it dissolves passes through the canvas into the electrolyte and is deposited on the graphite slabs under the tray. It is deposited in a highly crystalline form and scraped to the open end of the tank for removal. After washing it is melted.

The electrolyte is neutral silver-copper nitrate solution containing 60 grms. silver and 40 grms. copper (as nitrate) per litre. In some works the solution contains 30Ag, 20Cu, and free nitric acid up to 7 per cent. A current density of 50 amps. per square foot anode at 3 to $3\frac{1}{2}$ volts is employed.

In the **Moebius** process the anodes are suspended vertically by lugs in the electrolyte. Stainless (chromium) steel plates 12 by 20 by $\frac{1}{16}$ inch are employed as cathodes. Mechanically operated wooden blades attached to an oscillating rack are used to scrape the deposited silver crystals from the cathodes and prevent short circuiting. The detached silver falls into a wooden tray for removal. The current density is similar to that for the Thun process. The advantages of the Moebius process are (1) *both* sides of the anode are attacked; (2) better circulation of the electrolyte; (3) mechanical scraping of the cathode is possible. On the other hand, it must be stopped to

remove silver (in large units at any rate) and a good deal of scrap may be made. Maintenance costs are high.

The Thun process can deal with any shape or weight of anode, and they can be completely corroded, fresh anodes being laid on the remains of the old ones.

The gold accumulates round the anodes as a black slime which may contain particles of silver and basic copper salts. It is removed as desired by washing out the muslin lining or anode sacks. The solution is filtered and the mud boiled with water containing a little free sulphuric acid to remove copper salts. After settling, the liquor is syphoned off and the mud dewatered in a centrifuge, washed and dried. It is boiled for three hours in 80 per cent. sulphuric acid to remove copper and some silver, leaving a gold residue which may assay 970 fine.

Melting of Silver Crystals.—The crystals are thoroughly washed with water and melted in crucibles. In the silver works special furnaces of a tilting type are used. The fineness for the standard fine silver market—999 fine—is made by adding a little copper to the melt.

Refining the Gold.—The finely divided gold obtained in parting—gold sand—when cast into anodes for electrolytic refining may be 980 fine. The remainder is silver. The gold, melted in crucibles, is cast into anodes in closed moulds 9 by 5 by $\frac{3}{8}$ inches, each weighing about 140 ounces troy. The **Wohlwill** process is carried out in a stoneware cell 20 by 12 by 12 inches. The anodes are suspended in pairs from silver rods crossing the top of the cell. The cathodes are fine gold strips 2 inches wide and 0·003 inches thick, 12 inches of which is immersed in the electrolyte, hung in rows of four across the cell. The cell contains 3 or 4 pairs of anodes sandwiched between the cathodes.

The electrolyte is a solution of gold chloride. It contains 80 to 100 grams of gold per litre and 10 per cent. free hydrochloric acid, and is kept in circulation by air lift.

A minimum temperature of 140° F. is maintained by a steam coil contained in a lead-lined box in which the electrolytic cell is packed in sand.

The current density is 125 amps. per square foot of anode surface at $1\frac{1}{2}$ volts.

Pure gold deposits in a somewhat warty crystalline form firmly adherent to the cathode. After thorough washing the gold is dried, melted down in new crucibles, and cast into bars weighing 700 to 800 ozs. each. The metal has a fineness of over 999·7.

The anode scrap, amounting to about 5 per cent. of the total, is melted down with the gold sand and re-cast.

The silver in the anodes forms chloride and falls as a mud to the bottom, carrying with it varying amounts of gold. The gold is removed by boiling the precipitate with aqua regia, and the gold chloride produced is used to maintain the strength of the electrolyte. The silver chloride is sent for reduction to the doré furnace.

Platinum.—Platinum present in the anodes goes into solution in the electrolyte and does not interfere. The electrolyte may contain up to 60 grams per litre. It is recovered by oxidation with nitric acid and precipitation with ammonium chloride, *e.g.*

$$2NH_4Cl + PtCl_4 = (NH_4)_2PtCl_6$$

The salt is heated to decompose it, and form platinum sponge.

Toughening Brittle Gold.—Mere traces of arsenic, antimony, bismuth, and lead suffice to render gold brittle. It is toughened by treating the molten metal with mercuric chloride, or by passing chlorine through it by means of a clay tube, as practised at the Royal Mint (**Miller's process**). The bismuth, arsenic, and antimony chlorides volatilise. If silver be present, the silver chloride formed fuses and rises to the top. The gold is not attacked, gold chloride being decomposed at high temperatures. This process is also used for parting alloys containing little silver.

Smelting with Lead.—Old crucibles that have been used for gold and silver melting are first picked over, ground, and amalgamated. The residues are then smelted with lead-yielding materials, and the resulting metal cupelled to extract the gold. "Sweeps" (sweepings) is similarly treated. Ores are also sometimes smelted with lead.

Alloys.—The common method of expressing the quality of a gold alloy is in "carats" and carat-grains (4 c.g. = 1 carat).

Pure gold is 24 carats fine; 18-carat gold contains $\frac{3}{4}$ gold and $\frac{1}{4}$ alloy, or 750 parts per thousand; 9-carat gold, 375 parts per thousand. English-coinage gold is 22 carat, or 916·6 parts per thousand. Its specific gravity is 17·157. The alloy is copper, which is added to harden it. A new sovereign[1] weighed $123\frac{1}{4}$ grains, but was legal tender so long as it did not fall below $122\frac{1}{2}$ grains, $\frac{3}{4}$ grain being allowed for wear. The French and United States standard alloy is 900 fine, or 21 carats $2\frac{3}{8}$ carat-grains. The terms "worse" and "better" are applied as in silver. Thus the above alloy is 0 carat $1\frac{5}{8}$ carat-grains worse than English gold.

Articles of gold jewellery down to 9 carats are stamped by the Goldsmiths' Company with a Hall-mark, indicating the quality, the year of production, and the Assay Office at which the tests were made.

Copper and silver are usually alloyed for the purpose of hardening gold, when malleability is required for purposes of working. Zinc is sometimes added when rigidity and hardness are most important. Pencil-cases and watch-chains often contain the latter metal.

White Gold.—Used in imitation of platinum for jewellery is an alloy of gold with palladium.

[1] Alas! alas!

CHAPTER XVII

TIN

Physical Properties.—Tin is a white metal with a faintly yellowish tinge. It has a high lustre, and is very malleable. Foil $\frac{1}{1000}$ of an inch thick can be obtained by beating. It is ductile, but its tenacity is low—only about 2·1 tons per square inch. Its melting-point is 232° C., and it is not sensibly volatile at furnace temperatures if closely covered to exclude air.[1] Near the melting-point it is brittle, and a cake of tin heated till the edges begin to melt and then dropped on the ground breaks up into peculiar long-shaped, columnar pieces known as " grain tin." Tin which is impure does not readily do this. When bent, a strip of tin emits a peculiar crackling sound known as the *cry*. This is supposed to be due to the internal friction between the crystalline particles.

Tin is readily obtained in crystals, like antimony or bismuth. If the surface of an ingot or a tinned plate be treated with a mixture of sulphuric and nitric acids, beautiful crystalline markings make their appearance. This is known as the *moirée metallique*, and is used as a metallic ornamentation, being coated with coloured varnishes. The metal is a poor conductor of heat and electricity.

Pure tin, when cast in a mould, at a low temperature, solidifies with a bright metallic appearance ; but if impure, it presents a more or less frosted appearance, according to the amount of impurity present.

Commercial tin often contains small quantities of lead, copper, arsenic, antimony, and tungsten.

The metal is not affected by dry or moist air at ordinary temperatures. When exposed to low temperatures the metal sometimes undergoes a remarkable change, and is converted into a greyish powder—" grey tin." This change may occur at temperatures below —39° C. Heated in air, tin oxidises, forming stannic oxide (SnO_2). It combines readily with sulphur, forming stannous sulphide, SnS. This when calcined does not form sulphate, but yields SnO_2 and SO_2. SnS is decomposed when heated with metallic iron. Tin dissolves in hydrochloric and sulphuric acids. Nitric acid acts violently on it, and converts it into an oxide. It is also soluble in caustic soda and potash, forming soluble stannates. It combines with iron at red heat, forming a brittle compound FeSn.

It is not readily attacked by vegetable acids or animal juices, and

[1] Tin is non-volatile at ordinary furnace temperatures, but volatilises at the temperature produced by its own oxidation when burning in a muffle.

tin plate is hence largely employed in the canning industry. For the same reason it is used for coating the interior of vessels for cooking purposes.

Ores of Tin.

Cassiterite—Tinstone (SnO_2).—This is the only important ore of tin. It is yellowish-brown or black in colour, and occurs crystallised and massive, in well-defined veins, and in grains, sometimes distributed through a mass of rock, such as granite. It has a specific gravity of 6·5 to 7. It has a high lustre, and is too hard to scratch with a knife. In the vein it is associated with galena, blende, copper, and iron pyrites, arsenical iron pyrites, and other minerals. Wolfram (tungstate of iron), another remarkably heavy mineral, is also associated with it. A large number of non-metallic minerals occur as associates. Fluor, garnet, mica, chlorite may be mentioned in granite, gneiss, and porphyry. *Stream tin ore* is tinstone which has accumulated by the weathering of the rocks containing it. It occurs in alluvial deposits in large amounts in the E. Indies, Nigeria, Mexico, and elsewhere. The lighter materials have been removed by the action of running water, and the tinstone and associated heavy minerals left. *Wood tin* is tinstone showing concentric markings more or less resembling wood. Tin lodes are often very poor, sometimes not containing more than 1 per cent. of tinstone. Its high specific gravity facilitates dressing operations, and such ores, by careful picking, stamping, and washing, can be profitably worked. Tin ore is found in Cornwall and Devon, Germany, Spain, Russia, Malacca (Banca), Australia, United States, and Mexico.

The ore is carefully dressed by hand picking, stamping, and washing, to remove gangue. The copper and arsenical pyrites are not completely removed, and the wolfram also remains with the tinstone.

Bell-metal ore, or tin pyrites, is a mixture of copper, iron, and tin sulphides.

Smelting.—The ore is first carefully calcined in a large, low, reverberatory furnace, being turned over every 20 minutes or so. In Brunton's calciner the bed is circular, and revolves on a vertical axis, the turning over being done mechanically. In roasting tin ores a moderate heat is necessary at first, to avoid clotting of the sulphides present.

During roasting the arsenic combines with oxygen, and is converted into white arsenic (As_4O_6), which is volatilised and deposited in long flues provided for that purpose, from which it is collected. Sulphur burns off as SO_2, and the copper is largely converted into sulphate.

The ore after this roasting is moistened, and left in a heap for a few days, to allow more soluble sulphates to form. It is then thrown into a tank and agitated with water. Copper sulphate and other soluble matters are dissolved, and the sediment consists mainly of stannic and ferric oxides. The lower layers contain the larger proportion of oxide of tin owing to the greater rapidity with which it settles,

on account of its high specific gravity. The ferric oxide is separated by washing, and the concentrated oxide is known as *black* tin. It is sorted into various grades according to purity.[1]

Reduction.—In this country this is effected by heating the tin oxide mixed with carbon in the form of anthracite, in reverberatory furnaces, of the form shown in Fig. 154. The bed measures about 15 feet by 9 feet, and slopes towards the tap-hole *o*, outside which is the "float," or tin-pot; which is lined with clay to prevent the metal taking up iron. The stack is 40 or 50 feet high. The bed is of fire-clay resting on slate slabs supported by iron bars, and the fire-bridge is about 14 inches high.

The charge consists of about a ton of black tin mixed with about 3 to 4 cwts. (20 per cent.) of anthracite powder, according to purity. If silica be present a little lime or fluorspar is added as a flux. The mixture is damped to prevent dusting, and after introduction into the furnace the doors are closed and luted round. A low temperature is maintained for some time to ensure reduction of the tin oxide and prevent the formation of silicate. In 4 or 5 hours the charge is well stirred up, anthracite culm thrown in, and the charge again heated for another hour. After again rabbling, the metal is allowed to subside, and is then tapped into the float. The reduction takes place as follows—

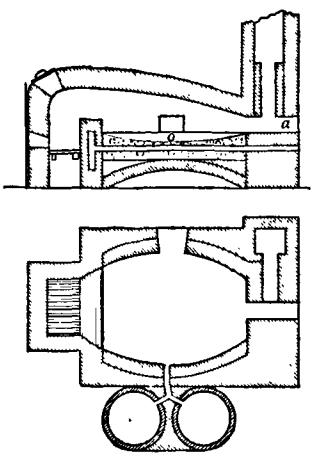


FIG. 154.—Furnace for smelting tin ores.

$$SnO_2 + C_2 = Sn + 2CO$$

A fluid slag, known by the smelter as "glass," runs from the furnace with the metal. It consists of silicates of iron, lime, and alumina. Oxide of tungsten is often present. It sometimes contains as much as 20 per cent. of tin. It is allowed to accumulate, and re-smelted to extract the metal.

A pasty mass, consisting of shots of tin, anthracite, and slag is left on the furnace bottom, and is raked out by the smelter. The tin contained in it is separated by stamping and washing.

The metal is ladled from the tin-pot into pig moulds, or, if pure, is run into the "boiling" pot.

Note.—Oil-fired furnaces and some modifications have been introduced. Slags are cleaned by iron scrap in a separate operation.

[1] **Removal of Tungsten.**—In the preliminary calcination wolfram is not affected. It is removed when necessary or desirable, by mixing the black tin with sufficient carbonate or sulphate of soda and heating in a special furnace to decompose the wolfram, yielding tungstate of soda and oxide of iron. The tungstate of soda is dissolved out by water and crystallised, and the oxide of iron removed by washing as before (Oxlands' Process).

The tin is recovered from the iron-tin alloy by adding it in regulated amounts to the furnace charge. The iron acts by reducing oxide and passes into the slag.

Reduction in Blast Furnaces.—Tin ore is also reduced in small blast furnaces, with charcoal as fuel. The materials are charged in at the top, and the furnace works continuously.

The loss of tin in the slags is much greater, but the tin obtained is very pure.

Smelting in blast furnaces is abandoned in this country, but in the East Indies and other places is still continued. About 32 cwts of charcoal per ton of tin are consumed in smelting.

Refining.—This involves two operations—liquation and boiling.

Liquation.—The pigs of tin, which weigh from 3 to 4 cwts. each, are piled on the hearth of a reverberatory furnace, with a bed somewhat more sloping than the reduction furnace, and heated carefully to the melting-point of tin. Some 18 tons of pigs are treated at once. The temperature is very carefully regulated. The purer tin melts, drains away, and flows out into the refining kettle. The impurities remain in an unfused state on the hearth, as a metallic, yellowish-white, hard, brittle mass, often porous, known as *hard head* It contains iron, tin, arsenic, sulphur, and a little copper. Sweating at a higher temperature yields a further quantity of less pure tin, which must be further treated.

Boiling.—The metal from the liquation furnace runs into the "refining kettle" in front. This is an iron pot about 4 feet 6 inches in diameter, heated by its own fire. Above the kettle is a lever attachment, by which logs of green wood can be held down in the molten metal. A steam jet is now employed in place of the logs.

The steam and gases disengaged by the action of heat agitate the metal and expose it to the air, and although tin is more readily oxidised than copper, bismuth, antimony, or lead, a scum of dross, consisting of iron, sulphur, arsenic, etc., forms on the top and is removed from time to time.

This is continued for from 1 to 8 hours, according to purity and the quality of tin required. For grain tin it is prolonged. This process is less an oxidation process than the effect of cooling at the surface, of metals less fusible than tin, which collect and form the scum. *Tossing* consists of lifting the metal from the pot in ladles and pouring it back again from a height of several feet. This is sometimes done instead of boiling.

For "common" tin the metal is ladled into the moulds, usually of granite, while boiling. For grain tin the metal after boiling is allowed to stand. The impurities yet remaining subside, and the upper purer layers are devoted to this purpose. The lowest layers require liquating again. Grain and refined tin are made from purer ores than common tin.

The purity of tin is tested by casting a small ingot in a stone mould. When pure, the edges are well rounded, and the surface remains

brilliant when cold. Frosting of the surface on solidifying is an indication of impurity.

Manufacture of Tin Plate.

The principal uses of tin are the manufacture of alloys (see p. 343) for making tin plate, tinning cooking utensils, and for tinfoil.

Tin plates are sheets of iron or mild steel coated with tin. The metal readily alloys with iron, and when heated somewhat above its melting-point, will adhere to a clean iron surface, forming at the surface of contact an alloy with the iron,[1] to which a thin film of tin adheres. The adhesion of the film of tin depends on the homogeneity and purity of the iron employed, soft pure metal being most readily tinned. Such plates are also best suited for the use of the tinsmith, being more readily bent and worked.

The plates are rolled from "tin bars." These are about 6 inches wide and $\frac{3}{8}$ of an inch thick. They are cropped into 15-inch lengths, reheated, and rolled square. They are again reheated and rolled to about four times the length by chilled rolls. The plate is doubled on itself, reheated, and again rolled, again doubled, reheated, and rolled, and so on. The compound sheet passes through the mill as one sheet, sometimes as many as 32 thicknesses being rolled together. The sheets are cut to the required size and separated. A little coal-dust is sometimes sprinkled over the plates to prevent them sticking together, and the reheating is carefully managed to avoid overheating and consequent sticking.

Formerly iron of special quality, smelted and refined with charcoal, was employed, but open-hearth steel is now generally used.

Preparation of Plates.—(1) The sheets of iron (black plates) are carefully annealed at a red heat. This is often dispensed with.

(2) They are then pickled in weak sulphuric acid at about 100° F., for about 20 minutes, well scoured with sand, and washed to remove scale (bright plates).

(3) The plates are annealed at a cherry-red heat in wrought-iron boxes from 10 to 12 hours, the air being excluded.

(4) The plates are cold rolled under chilled rolls to give a uniform, smooth surface.

(5) A second annealing of shorter duration and at a lower temperature than the first to remove the hardness produced by rolling is sometimes given.

(6) Another pickling in weaker acid than before, followed by scouring and washing to remove the thin film of oxide formed in the annealing processes.

The plates are then placed in water or lime water until required.

Tinning.—The sheets are first placed in a grease-pot containing melted tallow or palm-oil, somewhat strongly heated, and left till all the water has been driven off and the plates are uniformly heated and coated with grease.

[1] $FeSn_2$ (Hoare).

From the " grease-pot " they pass into a hot bath of molten tin (tinman's pot), covered with grease or with zinc chloride, and strongly heated. Here the alloy on the surface is produced. It next passes to the " wash-pot," which is divided into two compartments, and contains tin, but at a lower temperature. In the first compartment the coating of the tin is rendered uniform. The plates are lifted separately, and the surface brushed over with a hemp mop, and examined by the workman. If satisfactory, the plate is dipped rapidly into the second compartment, which contains pure tin, to remove the marks of the brush. It is then transferred to a grease-pot, where it passes through a pair of rolls, which squeeze off the excess of tin and improve the surface. The plates are then cleaned from grease in bran, rubbed with chamois leather or woolly sheepskin, and examined, faulty plates being rejected.

Formerly the plates, after tinning, were allowed to drain in a hot grease-pot, and the wire of tin which formed removed by immersion in a " list " pot, having about a quarter of an inch of molten tin at the bottom, in which the wire melted off.

Machinery has to some extent replaced hand labour for immersing the plates, particularly for large sizes and inferior qualities. The plates are carried through the several baths in succession by an arrangement of rolls and endless chain belts. *Terne* plate is an inferior quality coated with a lead-tin alloy.

The manufacture of sheet metal for tin plates is undergoing wide changes. Instead of rolling thin plates by repeated doubling " continuous " rolling mills are being built in which the steel ingots (or billets) are reduced to the required thickness by passing continuously through successive stands of rolls. In the later passes the metal is being cold rolled. Sheets of a much more uniform character are produced. For deep press work this is very important.

Tin plates are tested for porosity by exposure to hot water (for rusting) or by ferricyanide paper. The latter becomes blue where porosity exists. They give no reaction with the $FeSn_2$ crystal compound. In view of the speeding-up of modern practice, such testing is important.

Tinning Copper Articles.—The surface is first carefully cleaned, and the metal heated somewhat above the melting-point of tin, a little powdered resin or ammonium chloride is dusted over, and molten tin is then wiped over the surface with tow. A quarter of an ounce of tin will cover 2 square feet of surface, giving a durable coating.

Brass pins[1] are tinned by boiling them with cream of tartar, alum, salt, and granulated tin, in water. The tin is slowly dissolved by the liquor, and the zinc in the brass precipitates it on the surface.

[1] Most pins are now made of mild steel.

CHAPTER XVIII

ZINC AND ANTIMONY

THIS metal is commonly known as "spelter."[1] It has a bluish-white colour and high lustre. The brightness of the fracture is dimmed by impurity, notably by iron. Commercial zinc is highly crystalline, hard, and brittle. When pure, however, the metal is malleable, and ordinary zinc becomes sufficiently malleable to be rolled into sheets when heated to 120° to 150° C. If heated over 200°, the metal is more brittle than when cold, and can be powdered. It is harder than tin and softer than copper. It has a specific gravity of 7·1 when cast, but this may be increased to 7·2 or 7·3 by rolling. It fuses at 419° C., and is very fluid. It contracts very little in solidifying, and hence is suitable for castings. The nature of the casting is influenced by the temperature of pouring. If poured very hot, the castings are crystalline; but if near the melting-point, they are more granular. Zinc boils below[2] the melting-point of silver, 950° C., and the vapour burns in air with a bluish-white and very brilliant flame, forming oxide of zinc (ZnO); but ignition may occur at temperatures above dull redness, due to local high temperature developed by the oxidation of the metal itself.

Note.—In view of the recovery of zinc as vapour the latent heat of liquefaction and vaporisation are important. The former is 22·6 and the latter 425. Owing to the high latent heat the condensation is not readily completed. The condensers must be kept hot enough to maintain the metal in a molten state. Rapid cooling of the vapour increases the amount of zinc fume—blue powder—which does not readily melt, and diminishes the amount of spelter. The temperature of the condensers is about 500° C.

The tenacity of cast zinc is 1·25 tons. After rolling and annealing zinc has a tenacity of 7 to 8 tons, and wire, 10 tons per square inch. The elasticity is high. Rolled zinc retains in some measure its malleability, and the hardness induced is removed by annealing at a *low* temperature. Zinc was formerly solely used for brass-making, the fact of its being malleable when slightly heated having been discovered early in the nineteenth century. The first rolling-mills were erected in Birmingham.

A little lead (under 1 per cent.) added to zinc intended for rolling is of advantage, but this renders it unsuitable for making strong brass.

Zinc alloys with aluminium are in extensive use.

Chemical Properties.—Above its boiling-point zinc burns to

[1] Brazing spelter is an alloy of equal parts of copper and zinc.

[2] About 930° C.

ZnO—" philosopher's wool." Thus produced, the oxide is in a light, feathery condition, hence the name. It is white, non-volatile, and infusible at furnace temperatures, but becomes yellow when heated, and at very high temperatures agglutinates. It combines with silica and forms a very refractory silicate. The oxide is reduced by carbon monoxide, carbon, hydrogen, and iron at temperatures above its boiling-point. Like iron, zinc is oxidised by carbon dioxide and by steam.

Pure zinc is not acted on by water, and but slowly by dilute sulphuric and hydrochloric acids, but readily dissolves in nitric acid.

Zinc precipitates gold, silver, copper, platinum, bismuth, antimony, lead, tin, mercury, and arsenic from solution.

It does not readily combine with sulphur, but the sulphide is obtained by heating the oxide with sulphur, or by projecting a mixture of zinc-powder and sulphur into a red-hot crucible, ZnS being formed. This sulphide is practically infusible, and on roasting behaves like copper and lead sulphides, sulphur dioxide is evolved, and sulphate and oxide of zinc formed. A higher temperature is required to decompose zinc sulphate than is required for iron, copper, or silver sulphates. Zinc sulphide is sometimes removed from ores by roasting at a low heat, and drenching the roasted mass with water to dissolve out the soluble sulphate of zinc formed. Sulphide of zinc is reduced completely by carbon and iron at high temperature, the zinc being volatilised.

Galvanised Iron.—Zinc is little affected by ordinary atmospheric influences. On exposure to moist air it becomes coated with a film of oxide of zinc, which, being insoluble, protects the metal from further action. This property is applied in coating iron articles with the metal by dipping them in a bath of molten zinc, the process being known as *galvanising*. Before dipping, they are pickled in dilute hydrochloric or sulphuric acid, to remove the scale, and afterwards scoured, if necessary, and washed. They are then introduced into the molten zinc, covered with sal-ammoniac,[1] which acts as a flux. Tin and lead are sometimes added to the bath, to improve the appearance.

Electro—cold galvanising—is being successfully introduced. Flexible electrodes are necessary to ensure a uniform coating.

Sherardising is a method of coating iron with zinc by heating it at 250°–400° C. embedded in powdered zinc admixed with some oxide. A thin but very firmly adherent and even coating of the metal is produced. Its uniformity enables finished work to be treated in this way. The material is heated for some hours, and at the temperature employed distortion is avoided and there is little if any loss in strength, which invariably occurs in hot galvanising, *i.e.* dipping.

Zinc is superior to tin as a coating for iron for atmospheric work,

[1] This produces some zinc chloride and the mixture floats as a coating on the bath. In modern practice other substances, including cyanogen compounds, are often added.

as it is electro-positive to iron, and if the iron is laid bare at any point, the electric conditions set up result in the zinc being dissolved and the iron preserved. Tin, on the other hand, assists in the more rapid attack on the iron at the bare place, owing to its being electro-negative. Zinc being, however, readily attacked by vegetable acids, and also by alkalies, it cannot be used in contact with those bodies, nor in canning meats, fruits, etc. In towns where sulphurous acid and other acid vapours exist in the atmosphere, both zinc and galvanised articles are readily attacked. Salts in solution cause the action of water on it to be more rapid. The purer the zinc the less rapidly this occurs.

Zinc Ores.

Red Zinc Ore.—Spartalite—zincite (ZnO)—is generally red, owing to the presence of manganese. It is found associated with franklinite at *Franklin, New Jersey.*

Calamine—carbonate of zinc—($ZnCO_3$)—varies in colour, from white to brown. The brown colour is due to oxide of iron. It is generally of an earthy character. Some specimens are like entwined reeds, hence the name. It occurs in Flint, Somerset, Mendip Hills, Alston Moor in Cumberland, Lead hills in Scotland, Tarnowitz, in Silesia, Rhine Provinces, and Belgium (Aix-la-Chapelle), in Spain, and in America. It usually occurs in limestone rocks, and is associated with the silicate. The Silesian calamines contain as much as 8 per cent. of silicate, and carry from 6 to 45 per cent. of zinc. Blende, galena, and sulphate of lead often accompany calamine. Lead and iron are both objectionable in zinc ores, on account of the corrosion of the retorts at the high temperature employed, by the oxides of those metals. Calamines are carefully dressed to remove lead as completely as possible before smelting.

Electric Calamine [1]—hydrated silicate of zinc—is found associated with the carbonate.

Blende—sphalerite—black jack—zinc sulphide (ZnS), is the commonest zinc ore. It varies in colour from pale yellow to black, and has a resinous lustre. Pure ZnS is white, and the dark colour of blende is due to iron and other impurities. It is generally dark-coloured and crystalline. It commonly occurs associated with galena and pyrites, in limestone and other rocks. It is separated by careful dressing (see "Flotation"). It occurs in North Wales, Derbyshire, Isle of Man, Cumberland, Cornwall, Freiberg, United States, Australia, Russia, and many other localities.

Extraction of Zinc.

Zinc is extracted in the treatment of simple ores, by the reduction of the oxide with carbon or carbonaceous matters, at a temperature above the boiling-point, so that the reduced metal is vaporised. The

[1] Calamine of Dana.

reduction is conducted in closed retorts, and the zinc vapour is led into condensers outside the furnace, and condensed. The discovery was made by Henckel, in 1721.

$$ZnO + C = Zn + CO$$

All ores are roasted to convert them into oxides, for although *carbonate* of zinc would readily reduce without calcining, the conversion of the CO_2 expelled from it into CO would entail a large consumption of carbon, and a large increase in the volume of gas escaping from the condensers, with consequent greater loss of zinc.

$$ZnCO_3 = ZnO + CO_2$$
$$CO_2 + C = 2CO$$

Calamines are readily calcined on the bed of a reverberatory furnace, or often by the waste heat from the smelting furnaces. In Silesia, the small ore is treated in reverberatory furnaces, and the lump ore in kilns into which it is charged at the top with a little coal, and withdrawn at the bottom. Care is taken to keep the temperature too low to reduce and volatilise the zinc.

In calcining blende it is necessary to reduce the sulphur below 1 per cent., as in the ordinary reduction process zinc sulphide is not decomposed. It follows that each 1 per cent. sulphur entails a loss of 2 per cent. zinc. Owing to the ease with which zinc sulphate is formed during the calcination it is necessary to finish the calcination at a high temperature, 900° C., in order to decompose it before passing to the retorts.

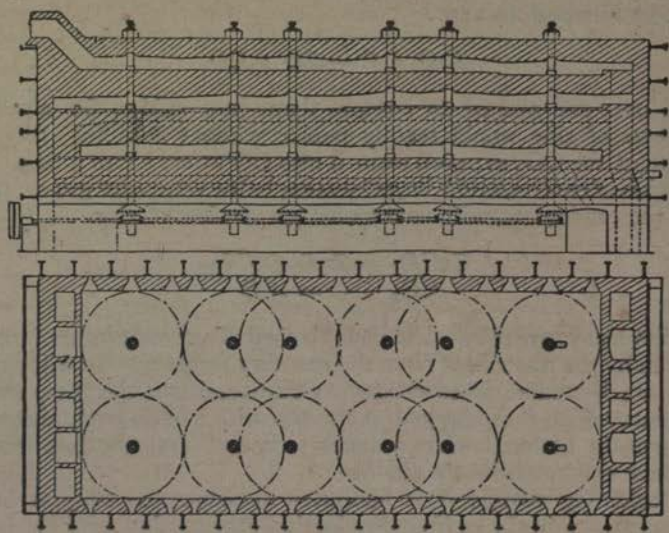
$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2$$

The operation is usually carried out in multiple-decked long-bedded furnaces provided with mechanical rabbles so operated that they move the material gradually along the furnace bed. The beds communicate at alternate ends, so that the ore admitted at the top is gradually moved downwards and towards the fireplace, with constant rabbling. When it is desired to utilise the sulphur dioxide formed for the manufacture of sulphuric acid, the furnace is of the muffle type. Fig. 155 shows such a furnace. It will be seen that the two lower beds are heated beneath but the upper bed relies for its heat on the sulphur in the ore freshly admitted at the top, in addition to that carried by the gases from the lower beds.

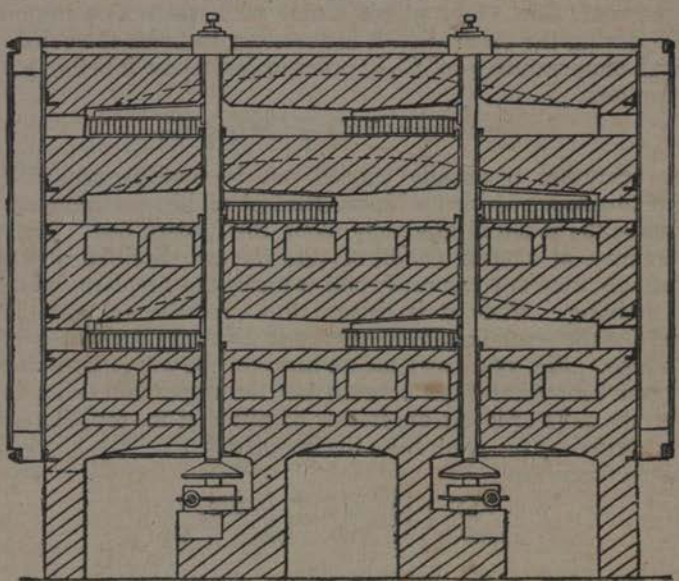
The reactions are—

$$ZnS + 3O = ZnO + SO_2$$
$$2ZnSO_4 = 2ZnO + 2SO_2 + O_2$$

The reduction of the calcined ore is effected in closed vessels, crucibles or retorts, connected with suitable condensers. It is important (1) that the condensers should be of ample size, (2) that the exit for the gases should be contracted so as to prevent the oxidation



Longitudinal Section and Plan.



Transverse Section showing Heating Flues and Rabbles.

FIG. 155.—Ridge roasting furnace for zinc blende. Muffle type.

of the zinc distilled off by the entrance of air into the condenser; (3) that the gases in the retorts and condenser should contain as little CO_2 as possible, or oxidation of the reduced metal will occur. To this end a high temperature and excess of carbon are necessary.

English Process.—In this process, introduced by Champion, at Bristol, early in the eighteenth century, the zinc ore (calamine) was mixed with carbon, and heated in large fire-clay crucibles, 4 feet high and 2½ wide at the top, having a hole in the bottom, to which a sheet-iron pipe, 6 inches in diameter, passing through the bottom of the furnace into a vault below, was applied. The lids of the pots were cemented on. The zinc vapour descended and was condensed in the tube—"Distillation per descensum." The method is wasteful and has been entirely abandoned.

The Carinthian Process was somewhat similar, but fireclay tubes were employed instead of crucibles. The zinc condensed in the lower part of the tube which projected through the furnace bottom. The process is not now employed.

The Belgian Process was introduced in 1810. It is conducted in cylindrical or elliptical retorts closed at one end and open at the other. They are about 39 inches long, 8 inches in diameter, and are supported at the ends, resting on the back and front walls of the furnace. They are somewhat inclined to the front, the open end being the lower, and are arranged in tiers one above the other.

Figs. 156, 157, show the arrangement. A (Fig. 156) is the furnace chamber—the back wall being vertical, with projecting ledges on which the ends of the cylinders rest. B is the fireplace; *c* the flues. The front of the chamber is closed by a cast-iron frame, D, protected on the inner side with fire-brick. Each of the compartments of the frame holds two retorts, which lie with their mouths resting on the framework. Each furnace holds from 40 to 80 of such retorts, and they are built in blocks of four, back to back, with a common stack. The metal is condensed in fireclay receivers of the form shown in Fig. 158; one of which is adapted to the mouth of each retort. A sheet-iron cone with a small aperture fits on this to condense fume. Before their introduction into the furnace, the retorts are carefully heated to redness. The spaces in the front frame are stopped with clay (cement of ground pots and raw clay), and the temperature gradually raised during 12 hours, the mouths of the retorts being loosely stopped with clay plugs.

The charge is a mixture of calcined calamine or blende with carbonaceous matters—anthracite or other non-caking coal, coke-dust, etc., as finely divided as possible, and slightly moistened. It is introduced by means of a scoop with a long handle. Each retort receives a charge of from 30 to 60 lbs., the lower ones, being most strongly heated, receive the heavier charges.

After charging the condensers are adapted (resting on a brick) and luted round. As soon as distillation commences, the fume-condensers are put on, a wet rag being often applied at the joint

to prevent escape. The operation is judged by the flame of carbon monoxide which is ignited, and burns at the small opening at the mouth of the fume-condenser. At first the fumes are brown, and result from the cadmium in the ore, which is reduced first. This is succeeded by the greenish-white characteristic zinc flame, with white fumes, which continues as long as the operation lasts. The metal is scraped out of the condensers, which are hot enough to keep it molten, at intervals; the fume condenser is removed for

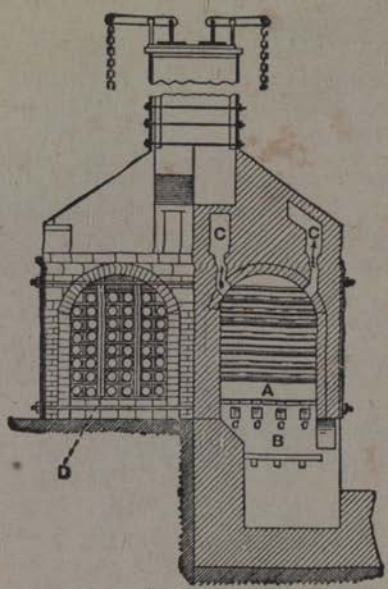


FIG. 156.—Belgian furnace.

FIG. 157.—Belgian furnace.

this purpose. The distillation occupies about 12 hours. When completed, the residues are raked out of the retorts into the pit below, and recharging commences.

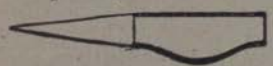


FIG. 158.—Condenser with fume-condenser attached.

The yield of zinc by this process from ore containing 50 per cent. varies from 30 to 40 per cent. About one-half the remainder is recovered from the residue (fume, etc., caught in the fume-condenser), and the rest is lost, mainly as vapour, partly due to imperfect condensation and partly to cracked retorts, etc.

The fume is marketed or returned to the retorts for reduction.

The zinc is received from the condensers by a large iron ladle, and, after skimming, is cast into ingots. Gas firing, with regenera-

tion, has now become common. The Hegeler and Dor-Delattre furnaces are modified gas-fired furnaces of the Belgian type.

Silesian Process.—The retorts employed in this process are ⌓-shaped, and are supported throughout their length, thus permitting of the employment of a more intense heat without collapsing. They are about 39 inches long, 8 wide, and 12 to 18 inches high. One end of the muffle is closed. At the other end an opening at the top is provided for adapting the condenser, and another below for introducing the charge. This is, when working, closed by a flat fire-clay stopping.

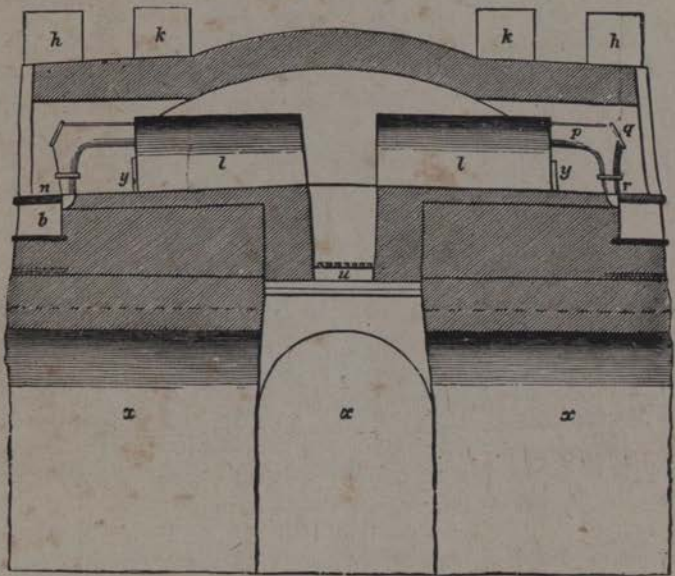


FIG. 159.—*l*, muffles ; *y*, charging door ; *p*, condenser ; *b*, receptacle for zinc ; *n*, fireplace ; *x*, vaults.

The loss of zinc in this process is somewhat greater than in the Belgian (though the residues contain less zinc), owing to greater leakage by cracking of the retorts.

Gas firing has now superseded the use of solid fuel. The type of furnace used is one in which the producer is attached to the furnace, the gas passing directly into the furnace chamber, or into a small combustion chamber, prior to entering the furnace. The air supplied for its combustion is heated by circulating through flues under the bed, heated by the waste heat from the furnace. Chambers for the calcination of calamine and the preliminary heating of muffles are also sometimes arranged to be heated by waste gases from the furnace.

In **modern zinc retort furnaces** both elliptical and ⌓-shaped retorts are used. Where both are employed the ⌓-shaped retorts

form the lower tier and are supported over the whole length. Usually the furnace has three tiers of retorts, the upper ones being elliptical. They incline forward as shown in the diagram. The retorts may be from 5½ to 9½ feet long and 13½ inches high.

The furnace shown in Fig. 160 is of the recuperative counter-current gas-heated type, the gas and air reaching the furnace by way of the recuperator chambers F. In this furnace special provision is made to keep the fronts of the retorts hot in order to prevent the formation of impervious plugs of the charge by the condensation of zinc and lead vapours in the charge near the exit and so avoid increased leakage

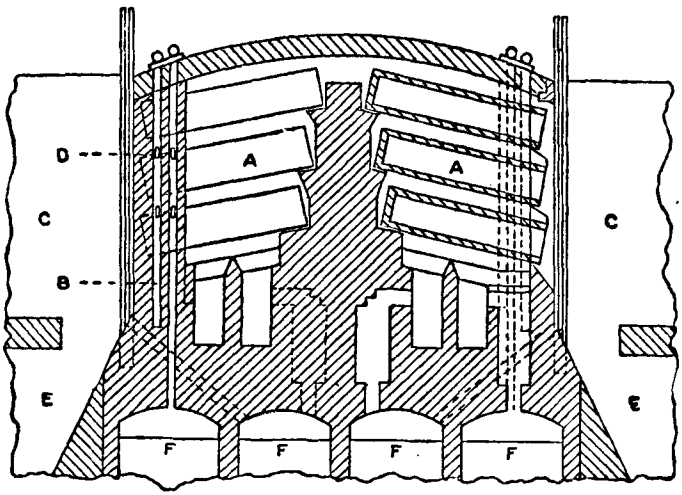


FIG. 160.—Rück furnace for zinc.

of vapour resulting from an increase of internal pressure and other troubles. Passages B and D convey separate air and gas supplies to the ports shown, opening just under the ends of the retorts to ensure full heating at that point. C is the condenser space, which virtually forms part of the furnace. It is often partially covered, and ensures a satisfactory temperature for condensation[1] and is always provided with iron apron plates which can be let down to protect the workman when raking out the spent residue into the pit E. The condensers employed are the type shown with sheet iron prolongs in Fig. 158. Only the conical prolongs or fume-condensers project beyond the line of the furnace.

Method of Working.—Great difficulties are encountered in making satisfactory retorts, and special means are adopted to secure refractory, tough, non-porous, highly conducting retorts with the minimum tendency to soften and sag at the temperature of the operation.

[1] Condensation at high temperature gives the maximum amount of fluid zinc, and minimum fume.

Careful selection and admixture of clays and burnt material is made,[1] and hydraulic presses of great power are employed in the manufacture to secure uniformity and freedom from porosity. The retorts are air dried and seasoned over long periods before use. Satisfactory retorts play no small part in the economical working of the process. When put into use they must be slowly heated. It is important that the materials used shall resist the attack of the lead and iron oxides and other compounds always present to a greater or less extent in the charge.

The **charge** consists of the roasted ore mixed with about 50 per cent. of its weight of anthracite or other coal with a high carbon content. The materials should be finely divided to ensure good contact between ore and reducing agent. The amount of carbon present should be sufficient to ensure the production of carbon monoxide only in the issuing gases, as zinc vapour is oxidised by carbon dioxide. The reduction is effected by both carbon and carbon monoxide, but if the amount of carbon is sufficient the dioxide is at once reduced if the temperature be maintained.

$$\begin{aligned} ZnO + C &= Zn + CO \\ 2ZnO + C &= 2Zn + CO_2 \\ ZnO + CO &= Zn + CO_2 \\ CO_2 + C &= 2CO \end{aligned}$$

The formation of the materials into briquettes has been attempted to ensure better contact and facilitate charging. A little common salt is often added. It is said to increase the amount of spelter.

As pointed out above, oxides of iron, manganese, and lead present in the ore attack the retorts. The amount present varies, but the charge should not contain more than 10 per cent., of which not more than 2·5 per cent. should be lead. Charges containing greater amounts are worked in some cases, but with greater difficulty, and in purchasing ores deductions are made if the amount be excessive.

The charge is introduced into the muffles either by means of a scoop-like shovel or by machine. In the former case each shovelful is thrown to the back of the retort and packed so as to fill the retort completely. A rod is then thrust through the material at the top of the retort to the back to make a passage for the zinc vapour and the condenser luted on. Its mouth is temporarily stopped. Mechanical chargers are of the nature of an endless conveyor band, which throws the material to the back.

When charging is complete the gas and air are turned on, and the temperature rises rapidly until a white heat is attained. The coal distils first and a luminous gas flame appears at the mouths of the condensers. When the reduction begins this is succeeded by the blue flame of carbon monoxide, which in turn becomes bluish-white when zinc vapour is present. The prolongs are then fitted and the distillation proceeds. If cadmium is present a brown smoke precedes the blue zinc flame.

[1] Carborundum retorts are also in use. Clay 1 part, coarsely ground carborundum 2 parts, with 10 per cent. moisture.

As previously noted, the condensation temperature is important, and as this depends on the furnace temperature, very careful regulation is necessary. It is maintained at about 1,100° to 1,150° C. Too high a temperature leads to loss of zinc; too low a temperature increases the amount of blue powder in the prolongs.

The molten zinc is removed at intervals by scraping it from the condensers and cast into flat ingots.

In modern zinc smelting the loss varies from 10 to 15 per cent., made up as follows: 4 to 5 per cent. as blue powder, 2 to 5 per cent. in the residues, 5 to 6 per cent. lost as vapour and through the breaking of retorts.

In case a retort breaks it is at once removed to avoid loss of zinc and also the formation of deposits of zinc oxide in the regenerators. The distillation occupies about 18 to 19 hours.

After the removal of the zinc the furnace is allowed to cool and the residues scraped into the pit in front. The residues from the front of the retort often contain zinc due to imperfect heating. They are collected separately and added to subsequent charges.

Reduction of Lead Contents.[1]—In the treatment of zinc ores containing lead, as much as 6 per cent. may be carried over by the zinc vapour. This is removed by melting the crude zinc in a reverberatory furnace with a slightly sloping bed, and provided with a well at the lower end, where a door for ladling out the metal is situated. By maintaining the temperature of the furnace just above the melting-point of zinc the lead—almost insoluble in zinc at its melting-point—settles to the bottom and collects in the sump. The nearer the temperature to the melting-point of zinc the more complete is the separation. The furnace holds a large amount of zinc—up to 20 tons—and as purified zinc is ladled out a fresh addition of crude metal is made. This takes place usually every twelve hours.

Zinc for rolling is thus treated, as more than 1 per cent. of lead seriously impairs its malleability. (Re-distilled zinc contains about 0·2 per cent.)

When the zinc contains much iron, a deposit of hard zinc is formed on the surface of the lead, and is separately removed. After melting the zinc the surface is skimmed to remove dross.

The purified zinc is ladled into iron moulds and the lead which separates is removed from time to time. It carries about 2 to 6 per cent. of zinc.

As the zinc retains from 1 to 1·5 per cent. of lead this process is only applicable to spelter containing over that amount of lead. The crude metal from the condenser in extreme cases may contain 6 per cent. of lead.

The removal of oxide of zinc and also of arsenic may be effected by the action of ammonium chloride. For the former purpose the salt may be melted on the surface only and the metal agitated; but

[1] Modern practice in ore dressing by flotation methods has made it possible to produce concentrates of zinc blende almost free from lead.

for the latter the salt should be forced below the surface, preferably in zinc tubes at a red heat.

Treatment of Ore containing Lead.—Several methods have been proposed to produce lead-free zinc from concentrates containing both metals. It was observed that in retorting leady ores there was always a tendency for condensation to occur near the mouth of the retort. The condensed matter deposited in the charge tended to choke the retort. Examination of this deposit showed it to contain much lead, and the zinc recovered was correspondingly purer.

This principle has been applied to secure prior condensation of the lead and purify the zinc by placing a filter of coke, brick, or other crushed porous materials in the mouth of the retort or by causing the zinc vapour to pass through a separate chamber filled with the material on its way to the condenser. The lead is retained by the filter. Lead interceptors are known as " dams " or filters, according to position.

Treatment of Zinc Fume.—The zinc fume which collects in the fume-condenser consists of oxide of zinc and finely divided metal. It is returned to the retorts and redistilled with carbon.

Vertical Retort Furnaces.—In modern methods older intermittent furnaces are being rapidly superseded by continuous vertical retort furnaces.

The retort consists essentially of three sections: (1) a heated section constituting the retort proper; (2) an upward extension; (3) a lower section provided with discharge apparatus.

The heated section is a rectangular chamber, 5 to 7 ft. in length, 1 ft. wide and 25 ft. high. The walls are built of special carborundum refractories, designed so as to permit of expansion without the escape of zinc vapour. This chamber is heated intensely, approximately to 1,300° C, by surrounding flues.

The upper section is of refractory brickwork. It is provided with charging apparatus and acts both as a preheater and filter for any zinc oxide or other fume. Additions of material are made from time to time.

The lower section is of iron and unheated. It is provided with roll-discharging devices for removing the spent material, and means for the introduction of an upward gas current to carry away the heavy zinc vapour. It is water sealed.

The condenser communicating with the top of the retort at the bottom of the upper section is of two parts: (1) an inclined rectangular conduit; (2) a large rectangular container—the sump. Both are lined with carborundum refractory and provided with baffle plates to regulate the movement and cooling of the gases. The sump has a tapping hole on the side remote from the retort. It has a capacity of 1–1½ tons. The condenser is carried on an elevated platform. Above this is the charging platform.

The charge consists of small briquettes made by thoroughly mixing the roasted ore and by-product with anthracite, caking coal, tar and sufficient water. The mixture passes through machines and the briquettes after drying are carefully coked in vertical kilns by hot gases from the retort flues. Excess of carbon is used and the coked briquettes do not alter much in shape or size during the passage through the retort. This ensures uniformity of working. Inert non-oxidising gas introduced at the bottom sweeps the products of distillation upward toward the condenser. Any dust or zinc oxide is removed by the upper part of the charge.

Operating continuously the volume, temperature, and zinc contents of the gases are fairly uniform and the large condenser can be operated with minimum formation of " blue powder." Gases from the condenser are drawn through scrubbers, the suction being carefully regulated. They consist largely of carbon monoxide and are burnt in the combustion chamber surrounding the retort.

"Dust" recovered from the condenser and scrubbers may amount to 8 per cent. of the zinc in the charge.

The condensed zinc is tapped into ladles and cast into slabs.

Wet Methods of Extraction

Many wet methods have been proposed for the treatment of complex ores containing large amounts of iron, copper, and lead, which cannot be roasted and treated in the ordinary manner owing to rapid corrosion of the retorts. The zinc, having been obtained in a soluble form, is precipitated as oxide by lime, and reduced, or the solution electrolysed.

Electrolytic Processes.—In these processes the zinc is converted into sulphate either by the careful roasting of blende (see p. 233) with the formation of the maximum amount of sulphate, or by dilute sulphuric acid acting on the oxide. There are a number of by-products containing zinc oxide. In roasting blende containing much iron the solubility of the zinc is diminished by the formation of zinc ferrate.

The solution obtained is submitted to electrolysis—after the removal of the iron and other impurities, notably cadmium, copper, lead, nickel, and cobalt, which seriously interfere with the deposition of the metal. Glue is often added to the solution to ensure uniform deposits.

Zinc or aluminium cathodes which revolve, and lead or other anodes are employed. After the recovery of a portion of the zinc the regenerated acid liquor is used for the treatment of further batches of material. Diaphragms of nitrated cellulose or other material are employed to separate the anodes and cathodes. The solution should not contain a large amount of free acid, as the quantity increases as the deposition proceeds.

Electrolytic zinc production has made enormous strides in recent years. In 1935 over 500,000 tons were so produced. The electrolytic plant at Traill (Canada) has a capacity of 400 tons a day.

Solutions of zinc chloride are also sometimes treated electrolytically. They are less easy to deal with.

The difficulties attending the production of dense coherent zinc are great. Spongy deposits entail great losses by oxidation in melting up the metal for casting purposes. In early processes, when the zinc was deposited on iron cathodes, the metal was thrown down in a soft spongy form from which the liquid was squeezed by passing between iron rollers. The loss in melting was enormous. Zinc of 99·95 per cent. purity may be obtained by electrolysis.

Electric Reduction Furnaces.—Where "water power" is available, as in Sweden, electric furnaces are in use. Usually the zinc condenses as blue powder and a spelter high in lead. The amount of the latter metal carried over owing to the high temperature is large. The products are redistilled for market.

ANTIMONY

The metal has a bluish-white colour and is highly crystalline and brittle. The surface of the pure metal exhibits beautiful crystalline fern-like markings, technically known as the "star." "Star" antimony is a guarantee of refined antimony. When iron and other metals are present the markings are absent and the crystalline surfaces of the fracture have a frosted appearance. Owing to improvements in methods of extraction the metal now produced is much purer than formerly. Fig. 161 shows the appearance of very good antimony. The specific gravity is 6·7 to 6·8, and the melting-point 632° C. At a white heat the metal slowly volatilises.

The metal combines with oxygen when heated. Three oxides exist: Sb_2O_3 antimony trioxide, Sb_2O_4 antimony tetroxide, and Sb_2O_5 antimony pentoxide. The trioxide is volatile *below a red heat*, and the pentoxide decomposes, forming the tetroxide, which is the stable form produced on heating. It is a white powder. It is used as a pigment.

Cooksons, C. brand.]

FIG. 161.—"Star" antimony.

The sulphide Sb_2S_3 is produced by combination of the elements when heated, and occurs naturally It is very fusible, and is volatile. When heated in air oxide of antimony is formed, but no sulphate (see Zinc). Its presence in mixtures of sulphides lowers the melting-point considerably.

Ores.—The principal sources of antimony are stibnite, the sulphide Sb_2S_3, which occurs as a lead-grey mineral with a very brilliant metallic lustre usually in elongated crystalline forms—needle ore—giving it a striated appearance. The mineral has a density of 4·63, and is soft enough to mark paper.

Oxides of antimony occur as senarmontite and valentinite—crystalline forms—and as antimony ochre and cervantite, usually in association with the sulphide.

Extraction.—In the older method of extraction the ore is concentrated by placing the hand-picked material in crucibles with perforated bottoms placed inside another, or on grids, and heating

sufficiently to melt the sulphide, which drained into the lower receptacle constituting crude antimony. This method is followed owing to the impossibility of treating the metal in the ordinary way by fluxing off the gangue.

The liquated product so obtained when heated with iron is reduced thus—

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb$$

The crude metal is heated under alkaline slags containing oxide and sulphide of antimony to remove the iron taken up in solution until it develops " star " on casting. This method is wasteful.

In the new methods the ores are calcined at temperatures sufficiently high to volatilise the sulphide and oxide, thus ensuring the removal of the antimony from the gangue. The volatile products which become almost completely oxidised are recovered in bag filters, or some similar appliance. Some lead and arsenic are carried over.

The recovered oxide is reduced by carbon, yielding a much purer product.

Uses.—The metal is principally used for hardening lead and tin alloys, and to a limited extent for addition to acid-resisting copper alloys. It is used in ornamental castings.

Antimony is soluble in lead when melted, but almost[1] insoluble in the solid state. Hence in alloys the separation of the harder metal embedded in the soft lead matrix produces a hardening effect. The low melting-point of the alloys makes them specially suitable for type and stereotype metals.

Antimony is also used for hardening tin, producing alloys which cast well. Up to 10 per cent. of antimony the alloys can be rolled. With larger amounts antimony forms a compound with tin $SbSn_3$.

White Metals for bearings consist of lead and tin alloys hardened by antimony, usually with the addition of copper.[2] The amount varies with the nature of the base of the white metal—lead base or tin base. The former are hardened lead alloys, and the latter hardened tin alloys. The antimonial compounds separate from the base in both cases, and form a hard skeleton, embedded in a softer base, on which the shaft is supported. The structure facilitates lubrication and uniformity of wear. Regulus metal used for taps, etc., in connection with sulphuric acid appliances is lead hardened with antimony.

Antimony is used to a limited extent in the manufacture of hydrochloric acid pumps, not being attacked by that acid in the absence of oxygen and oxidising agents. The old name for metallic antimony was " regulus of antimony." " Antimony " was sulphide of antimony.

[1] At ordinary temperatures lead only retains 0·25 per cent. antimony (see p. 369).

[2] See Fig. 11, p. 11. The large crystals are $SbSn_3$, the needle crystals are the copper alloy and the dark portion the entectic.

CHAPTER XIX

NICKEL AND OTHER METALS

NICKEL—a white, hard metal—is used to a considerable extent, on account of its resistance to atmospheric action and its whitening effect on copper, in the manufacture of German silver and in many alloys. It is also alloyed with steel. Platinite is a nickel-steel alloy containing 46 per cent. of nickel. Its coefficient of expansion is the same as glass. Nickel is malleable, ductile, tenacious, and weldable; fuses at about the same temperature as iron, and is affected in the same way by the same impurities as that metal. Its specific gravity is 8·8, and, like iron, it is magnetic.[1] It oxidises when strongly heated, and combines readily with sulphur and arsenic, and is soluble in acids. It is found with iron in meteorites. In nature it occurs principally in combination with arsenic and sulphur in **kupfernickel** and **millerite**, and in magnetic iron pyrites, or as a hydrated silicate of nickel and magnesia in **garnierite**.

Arsenical ores are concentrated much as in copper smelting for the production of a *speiss* (see p. 211).

The process of extraction from speiss is essentially a chemical process, the nickel being ultimately obtained as oxide. This is mixed with lamp-black and oil, the mixture compressed and strongly heated. The oxide is reduced by the carbon.

Sulphide ores—mainly sulphide of iron—such as the pyrrhotite which occurs in very extensive deposits at Sudbury, Ontario, containing from 1·5 to 2·5 per cent. nickel,[2] are smelted in water-jacketed cupolas for the production of matte. The same principles underlie the concentration of the metal as operate in the case of copper. If a mixture of nickel oxide, iron sulphide, and silica be heated, iron silicate and nickel sulphide result.

The pure nickel sulphide may be subsequently reduced by calcining to oxide and reducing with carbon, or the nickel may be extracted by the Mond process. Unlike copper, nickel sulphide and oxide do not mutually reduce each other.

Concentration of Nickel in Sulphide Ores.—The ores after dressing are calcined and afterwards smelted with fluxes in water-jacketed furnaces as in copper smelting. The matte contains all the nickel, cobalt, and copper together with iron sulphide and the precious metals.

This matte is capable of enrichment exactly as with copper mattes by oxidation and fusion or by Bessemerising. In practice it is

[1] It loses its magnetic properties at 320° C. Steel containing about 26 per cent. nickel is non-magnetic.

[2] This forms at present the main source of nickel

"Bessemerised." The final matte if free from copper may be immediately treated for nickel, but nickel matte cannot be blown to metal as in the case of copper matte (see below).

When that metal is present separation precedes the nickel extraction.

Mattes containing copper may be calcined to produce a mixture of nickel and copper oxides, which is reduced by carbon, producing a nickel copper alloy—natural **Monel metal**—an alloy containing from 64 to 70 per cent. nickel (usually 67 per cent.) with 26 to 36 per cent. copper, 0·3 to 2 per cent. manganese, and not more than 2·5 per cent. iron with traces of other impurities.

A typical nickel copper matte after Bessemerising may contain—

Nickel	46	per cent.
Copper	35	,,
Sulphur	18	,,
Iron	1	,,

Monel metal is also made by alloying the metals themselves.

Monel metal has a tensile strength of 35 tons, and, like all nickel alloys, possesses a high degree of elasticity, which is less affected by heat than in other copper alloys. [The latter is one of the most valuable properties of nickel alloys to engineers.] Its resistance to corrosion and chemical action is high, especially to fixed alkalies, and it is used in filter and other appliances used in the manufacture of caustic soda. Its resistance to atmospheric action is nearly equal to that of nickel. Silicon 2–4 per cent., is added for casting purposes.

The alloy contracts considerably on solidification and cooling, making its use for castings almost as difficult as steel. Further, it must be kept out of contact with carbon and silica during melting.

Separation of Copper from matte.—The Orford process for separating copper relies on the solubility of copper sulphide in fused sodium sulphide. Nickel sulphide is insoluble. The matte is smelted with sodium sulphate in a cupola. The coke reduces it to sodium sulphide. The fused products separate in layers. The insoluble nickel sulphide sinks. Two or three meltings remove the copper.

Copper is also removed by "dead roasting" the matte in a furnace, followed by treatment with dilute sulphuric acid. The oxide of copper dissolves, but only about 1 per cent. of the nickel. On evaporating the solution copper sulphate crystallises out. The residue, consisting of oxide of nickel and some impurities, is ready for reduction.

Nickel matte free from iron and copper may be reduced by calcining to oxide and heating with carbonaceous bodies, or the metal obtained by the Mond process.

Extraction from Garnierite.—The silicate is run down in small cupolas with gypsum (sulphate of lime) or alkali waste (calcium sulphide); a matte of nickel and iron sulphide is obtained. The iron is removed as in copper smelting, and the pure sulphide obtained is roasted to oxide and reduced as before.

Mond Process.—When freshly reduced nickel is brought into

contact with carbon monoxide it forms a volatile compound, nickel carbonyl $Ni(CO)_4$, the boiling-point of which is 43° C. This decomposes, when heated to a higher temperature, into nickel and carbon monoxide. In the Mond process the mixed oxides of iron and nickel produced by roasting the matte are exposed to the action of water gas (see p. 102) at a temperature below 300° C. in order to reduce the oxide of nickel without affecting the oxide of iron. The hydrogen in the gas is used in this reduction and CO_2 passes over.

This gas is passed over incandescent carbon to provide a supply of nearly pure carbon monoxide, which is brought into contact with the reduced metal at 50° C. in a volatilising tower. The nickel carbonyl vapour is led into a decomposer, a cylindrical vessel filled with nickel granules heated to 200° C. At this temperature the carbonyl decomposes. Nickel is deposited and carbon monoxide separated. This is passed back to the volatiliser. Special means are provided to keep the granules in circulation. When the granules are large enough they are withdrawn and passed out.

This is the most important process for the extraction of nickel.

If a nickel granule be ground flat it will be seen to consist of a number of coatings of varying thickness. These can often be separated like the layers of an onion.

Nickel is rendered malleable by the addition of small quantities of magnesium or manganese.

Cobalt

Formerly the principal uses of this metal were for colouring glass and glazes for earthenware. Its oxide gives a fine blue colour to glass. Its use in the metallic state was very limited. It is harder and more tenacious than iron, and is used to some extent for electroplating as superior "nickel" plate, and in alloy, for increasing the elasticity of bronzes. Its properties are similar to those of nickel and iron.

Alloys of cobalt are now in extensive use. Stellite is an alloy containing up to 75 per cent. cobalt, 16·5 chromium, with molybdenum, nickel, iron, etc., which is used for rapid cutting. It is cast into form. It has a melting-point of about 1450° C. An analysis yielded: Co, 59·5; Cr, 10·77; Mo, 22·5; Mn, 2·04; Fe, 3·11; C, 0·87; Si, 0·77; S, 0·08; P, 0·04.

Other steel alloys for tools and magnets contain cobalt.[1]

Cobalt is highly magnetic and retains magnetism to 1115° C.

The modern steel for permanent magnets used in electrical appliances may contain up to 35 per cent. of the metal. Cobalt is produced by the reduction of the oxide by carbon and electrolytically.

Tungsten

Tungsten is largely used in the manufacture of "air hardening," "rapid cutting" steels, which may contain up to 18 per cent. of the

[1] Cobalt is used as the cementing material for agglomerating the carbides of tungsten and of tantalum in "Widia" and other materials used for tipping tools and for dies. From 3–13 per cent. cobalt is used.

metal. It is also used for making filaments for incandescent electric lamps. The metal has a very high melting-point, 3267° C., and is infusible at ordinary furnace temperatures. It is brittle, but by working in a special manner it becomes ductile and very fine wires are obtainable. It occurs naturally as wolfram, tungstate of iron, a very heavy black mineral, associated with tinstone, and scheelite, tungstate of lime.

The metal is obtained by preparing the oxide and reducing it with carbon or hydrogen. Obtained in this way it is a heavy black powder. It may also be produced by the Goldschmidt reduction process and by reduction in electric furnaces.

Tungsten has a sp. gr. of 19·1.

Its introduction into steel is due to Mushet.

Carbide of tungsten, the effective cutting agent in tungsten "high speed" self-hardening steels is now made in electric furnaces and used for rapid cutting as "Widia" for tipping steel tools. An analysis gave tungsten 88, cobalt 5·1, carbon 5·75, manganese 0·05, silicon 0·09, nickel 0·08.

Manganese

The metal has no application in the arts, except in alloy with other metals. It is a hard metal, and takes a fine polish. Its colour is white. It oxidises quickly in moist air, and is dissolved by acids. Its affinity for oxygen is so great that the oxide is not reduced to metal when heated in hydrogen or carbon monoxide, only manganese monoxide being produced. The oxide is reduced when heated with carbon; the metal is also produced by the reduction of the chloride, in admixture with potassium chloride, by metallic magnesium or sodium in crucibles. In the Goldschmidt process, finely divided aluminium is mixed with the oxide to reduce it. It readily takes up carbon and silicon.

Rich alloys with iron—spiegeleisen, ferromanganese—and with silicon, silico-spiegel, for use in steel-making, are produced in the blast-furnace by smelting ores containing oxide of manganese.

Manganese steel contains upwards of 10 per cent. of the metal. It is very hard, whether rapidly cooled or not.[1] It is used for the hard parts of crushing appliances, rail crossings, etc.

Manganese is also used in the manufacture of bronzes and brasses, and in the production of alloys for electrical purposes, such as manganin and constantan.

Chromium

This metal is used in alloy. In steel, it confers increased elasticity and hardness. It is used in stainless iron and steel, in armour plate, shells, and in "high-speed" steel. With nickel it forms the Nichrome alloys, used as wire in electrical heating appliances, and for vessels for resisting oxidation and chemical action. Pure chromium

[1] For drilling, manganese steel is softened by heating to redness and quenching.

is more infusible than platinum, and is as hard as emery. It is permanent in air, and may be heated to redness without oxidation.

The metal is obtained by reduction of the oxide at high temperature with carbon or aluminium, by electrolysis of the double chloride of chromium and ammonium. Ferrochrome containing upwards of 60 per cent. chromium can be produced in the blast furnace by smelting chrome iron ore. Chromium is produced by the Goldschmidt process and in the electric furnace. Chromium is unattacked by nitric acid, but dissolves in sulphuric and hydrochloric acids.

Chromium plating is of recent introduction. It is permanent in air if non-porous or if the body metal has received proper treatment. It is deposited from hot solutions of chromic acid.

Magnesium

This is a brilliant silver-white metal, which, however, rapidly tarnishes in moist air. Its specific gravity is only 1·74. It is highly tenacious, about 14·5 tons per square inch. It fuses at about 800° C., and at a high temperature can be vaporised and distilled, like zinc. It burns in air with a brilliant white light, and is used for photographic and other purposes. Heated to 450° C. it can be worked, rolled, and pressed readily, giving forms of great exactness and sharpness.

It is malleable, but not ductile, except at elevated temperatures. It is used in conjunction with aluminium in the production of light alloys of great strength for aeroplane construction. Magnesium wire is made by *squirting* the metal, in a heated state, through holes in a steel plate. The ribbon is made by flattening the wire in heated rolls.

Minerals containing magnesium are abundant: magnesite, the carbonate ($MgCO_3$); and dolomite ($CaCO_3MgCO_3$); carnallite ($MgCl_2.KCl.6H_2O$), kainit ($MgSO_4.KCl.6H_2O$) and kieserite ($MgSO_4H_2O$) occur at Stassfurth.

The metal was prepared by decomposing a mixture of magnesium chloride mixed with sodium or potassium chloride, by metallic sodium, equal to $\frac{1}{5}$ or $\frac{1}{6}$ of its weight, in iron crucibles heated to redness, the resulting chloride of sodium dissolved in water, and the magnesium purified by distillation in a wrought-iron still, provided with a lid secured by a screw.

The metal is now produced by electrolysis of the fused chlorides—carnallite. (See Aluminium.)

Aluminium [1]

This metal, although fairly hard, is characterised by its extreme lightness. Its specific gravity when cast is only 2·56, which on rolling is increased to 2·68. It is highly malleable and ductile. Its tenacity is about 17 tons per square inch, and its elasticity is about equal to that of silver. At about 660° C. it melts, and contracts on solidifying.

In mass, it is unalterable in dry or moist air, at any temperature, but when finely divided, takes fire and burns on heating, forming

[1] Aluminium ranks fifth in output following iron, copper, zinc and lead.

the oxide Al_2O_3, which is not reducible by carbon at furnace temperatures.

It was formerly obtained by decomposing the double chloride of sodium and aluminium by metallic sodium.

Aluminium is produced by the electrolysis of alumina—oxide of aluminium (Al_2O_3)—dissolved in a molten bath of cryolite and other fluorides.

Cryolite is a readily fusible white mineral resembling ice consisting of the double fluoride ($AlF_3 3NaF$). It melts at 525° C., and is capable of dissolving alumina to a maximum of about 26 per cent. with a lowering of the melting-point. With 20 per cent. alumina the melting-point is 470° C. Mixed with other fluorides lower melting-points are attained. A mixture of 59 per cent. cryolite, 23 per cent. fluorspar, and about 18 per cent. alumina has a melting-point of 465° C.

Fluorspar—a much cheaper material—also dissolves alumina, but the melting-point of the eutectic with 26 per cent. alumina is 687° C. The M.P. of the cryolite fluor eutectic is 485° C.

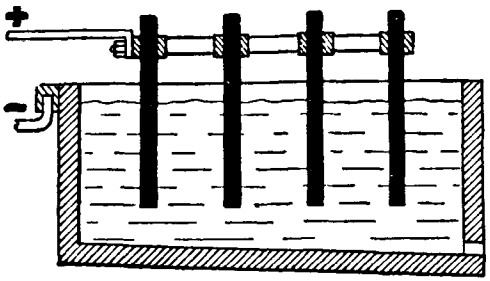


FIG. 162.

From these facts it will be seen that with a properly adjusted mixture a fusible bath of solvent can be made and the dissolved alumina decomposed by the current at a temperature which maintains the bath in a fluid state and permits the aluminium liberated to sink—about 900° C.

The temperature, fluidity, and density of the bath require constant attention. The heat necessary results from the resistance in the fluid bath. If the resistance rises owing to altered conditions of the bath—mainly insufficient alumina—a lamp in circuit indicates when the voltage exceeds 20.

Electrolytes vary in composition. Some contain free aluminium fluoride, and salt. In normal working the bath is partly covered by a crust of the solidified charge through which the anodes depend.

In the Heroult process the electrolytic cell is a carbon-lined iron tank (8 feet by 6 feet), connected with the source of electric current forming the cathode (negative electrode). The anodes are carbon rods which hang from an adjustable copper frame into the tank. A tapping hole is provided at the bottom for removing the aluminium.

In starting up, contact is made between the anodes and the bottom of the tank, and material is added round the contacts. When melted further additions are made, and this continued till the tank is filled. The metal as it separates sinks and is tapped as necessary. Oxygen is liberated at the anode, and either escapes or combines with the car-

bon to form CO and CO_2. The process is continuous, fresh supplies of alumina being added as required.

Although aluminium occurs in many minerals including clay, the principal mineral employed as a source of the alumina is bauxite,[1] and much care is taken to purify it (see p. 61).

The resistance to corrosion of aluminium is largely dependent on its purity, minimum sodium, silicon, carbon, and iron contents being important.

A current of some 700 amps. per square foot of bath surface (cathode) is employed with a drop of 5–7 volts per bath.

Attempts have been made to use plagioclastic Felspar (Labradorite) $Al_2O_32SiO_2(CaO.NaO)SiO_2$ and Leucite $Al_2O_33SiO_2 + K_2O.SiO_2$ by treatment with nitric acid to obtain preferential decomposition.

Aluminium forms many valuable alloys, see p. 346.

Aluminium is used in all kinds of domestic cooking and other vessels, for electrical conductors, aluminium bronzes, and in many light alloys and as a metallic paint.

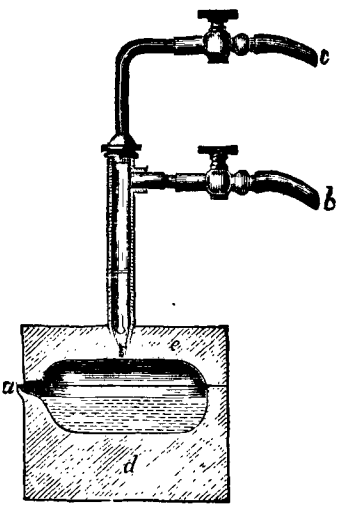


FIG. 163.—Lime furnace for fusion of platinum.

PLATINUM

This is a silvery or tin-white metal, almost as hard as copper. It is exceedingly malleable and ductile, being only inferior to gold and silver in these respects. Its specific gravity is 21·5. It is only fusible at the highest temperatures, *e.g.* in the oxy-hydrogen blow-pipe flame. It occludes oxygen like silver when molten. At a red heat it occludes nearly 4 times its volume of hydrogen. Its expansion by heat is 0·0000264 per degree, and is nearly equal to that of glass, 0·0000258. Wires can, therefore, be fused into glass without risk of breaking away—a point of great importance in the manufacture of electric lamps, etc. It welds when strongly heated.

Owing to its not being readily attacked by acids or chemical reagents, it was largely used for making chemical vessels, such as crucibles and dishes, stills for concentrating vitriol, parting, etc. Fused silica has largely taken its place for chemical purposes.

It occurs native, in grains in alluvial deposits, and associated with the rare metals, rhodium, osmium, iridium, ruthenium, palladium.

[1] The alumina is separated by heating the mineral with sodium carbonate, dissolving the sodium aluminate, leaving insoluble oxide of iron, and precipitating the alumina by agitation with added hydrated alumina or by passing CO_2 through the solution.

After chemical treatment, it is finally obtained as the double chloride of ammonium and platinum. This is decomposed by heat, leaving finely divided, spongy platinum, which is fused by an oxy-hydrogen jet in a small furnace made of blocks of lime (Fig. 163); or the ore is smelted with galena, and the lead obtained cupelled or dissolved in nitric acid leaving the platinum.

Electric arc furnaces are now used for the fusion of platinum.

Bismuth

This is a highly crystalline, brittle metal, of a white colour with a tinge of pink. Its specific gravity is 9·82. It melts at 268° C., and volatilises at high temperatures. The vapour burns with a bluish flame. It expands on solidifying.

Its principal use is for adding to alloys of lead and tin—whose melting-point it lowers—for making "quick" solders for pewter, and fusible alloys (see p. 344).

It occurs *native* and as *sulphide*. The metal is simply liquated out of the ores in which it is native, and the sulphide is decomposed by iron, sodium carbonate being used as a flux. A considerable quantity of bismuth is extracted from the cupels used for cupelling rich silver lead alloys containing the metal.

Cadmium

Cadmium is closely allied to zinc, with which metal it is generally found associated. It is more volatile than zinc, and in the distillation of that metal comes over first. The vapour burns in air, giving brown fumes of cadmium oxide, CdO—brown smoke of the zinc smelter.

Cadmium is being used as an addition in the production of sound copper ingots for wire bar, for deoxidation purposes 0·5 to 2·0 per cent. being used. It does not seriously lower the conductivity.

Cd. up to 0·5 per cent. increases the hardness and refines the grain of zinc for photozincographic processes. It is also introduced into certain white alloys for bearings and in aluminium solders.

Cadmium may be obtained by reduction of the oxide in retorts and condensing the vapour.

It is largely produced by precipitation from zinc solutions before electrolysing for zinc. In some cases zinc powder is used for the purpose.

A. V. Rhead precipitated the cadmium by aluminium in hot solutions—a much more efficient and rapid method—pure cadmium results.

Tantalum

This rare metal is being used for making filaments for incandescent electric lamps as a substitute for platinum and as carbide in tool tipping. Its melting-point is 2,830° C.

Ductile tantalum can be prepared by the thermal dissociation of the chloride on a glowing nuclear wire if foreign gases are rigorously excluded (Burgess and Basart), Z. Anorg. Chem., 1934.

CHAPTER XX

ALLOYS

WHEN metals amalgamate to form apparently homogeneous bodies when mixed in the molten state the substance is described as an alloy. Alloys may also be produced by the simultaneous deposition of two metals by electrolytic methods and by compression of powders in certain cases. The homogeneity may be often shown to be only apparent when examined microscopically. See Fig. 11, p. 11.

Many of the most important uses of a metal are as alloys.

When metals are melted together or mixed in the molten state they may :—

(*a*) Dissolve in each other in any proportions without combination;
(*b*) dissolve to a limited extent. In this case the degree of solubility may be greater at higher temperatures and diminish on cooling ;
(*c*) combine to form chemical compounds which may dissolve in the excess of metal at the temperature of melting ;
(*d*) remain undissolved. In this case they will separate in layers according to their specific gravities.

In the case of (*a*), (*b*), (*c*), the compound, or solid solutions of varying composition may separate on solidification and cooling, and in the case of (*b*) complete separation may occur. If still liquid, (*d*) will ensue.

Four common groups of metals which thus separate and do not form alloys are :—

Aluminium and lead.
Lead and zinc.
Copper and lead.
Copper and bismuth.

The three latter pairs may dissolve if strongly heated, but separate on cooling.

Influence on Melting-point.—As most alloys are cast the influence on the melting point and progress of solidification by the added metal is of first importance.

As will be seen on p. 369, if two metals form alloys the melting-point of the alloy is lower than the mean melting-point of its constituents. When each metal lowers the melting-point of the other the two branches of the liquidus converge and intersect at the point which represents the composition of the alloy having the lowest melting-point. This is the eutectic of the series. When more than two metals are present in the alloy eutectics are formed containing

all the constituents. When an alloy containing either metal in a larger proportion than the eutectic composition cools from fusion, solidification begins as soon as the temperature falls to or below that at which any separating component—solid solution or element—can be permanently solid. This separation commences when the liquid becomes saturated with this higher melting component and occurs in any alloy other than the eutectic when its solidifying point on the liquidus curve is reached.

The body thus separating contains a larger proportion of one constituent, leaving the still liquid portion richer in the other constituent which promotes fusibility, *i.e.* tends to leave a fluid residue of lower melting-point. This precipitation of solid will take place till a composition is reached which completely solidifies at the temperature to which the metal has cooled. In the case of all alloys in the eutectic range that temperature will be the melting-point of the eutectic. When solidification begins at a temperature considerably above that at which it is completed, it follows that there will be a tendency for variation of composition to exist between the parts which solidify first and later. Where the temperature falls slowly interchange between the solid and liquid occurs till solidification is complete, but rapid cooling may prevent this and the outer part of a casting may differ from the interior—the constituent depressing the melting-point being segregated towards the inner and hotter region. For this reason alloys containing less than the eutectic proportions sometimes show its presence in the interior. When no separation of components takes place during cooling and the metals remain uniformly diffused through each other when solid, the alloy is a simple solid solution. See Fig. 9.

The constituent metals present in a solid alloy may be associated in a variety of ways :—

(*a*) as elementary metals ;
(*b*) in solid solution or solutions ;
(*c*) as a eutectic ;
(*d*) as a eutectoid ;
(*e*) as compounds.

In the liquid state these may all be present in solution in the hot fluid metal and assume a separate existence during the cooling of the liquid, during the solidification or while cooling after solidification.

Thus lead in copper and its alloys may be in solution when hot, but separate on solidification. The low melting-point of the lead causes it to be moulded on the grains or distributed in minute specks through the mass. If a metal separates from another while fully molten it will float or sink according to gravity, but if solidification is in progress it will be entangled and remain mixed up with the other constituents.

Its effect will depend (*a*) on its melting-point and its behaviour on solidifying as in the case of eutectics (see below) ; (*b*) on its physical

properties, *e.g.* whether hard and brittle or otherwise; (*c*) on the extent to which it modifies or interferes with the uniformity of structure of the mass. Thus lead in copper-lead bronzes, on account of its softness, malleability and contraction on solidifying, makes such bronzes successful as bearing metals.

During such separation of metals on solidification the solidifying metal often assumes a dendritic form entangling the metal of lower melting-point.

Solid solutions, see p. 9. The more or less uniform diffusion of one metal in the other is the typical condition of a perfect alloy. Such perfect solution produces a structure similar to that of an

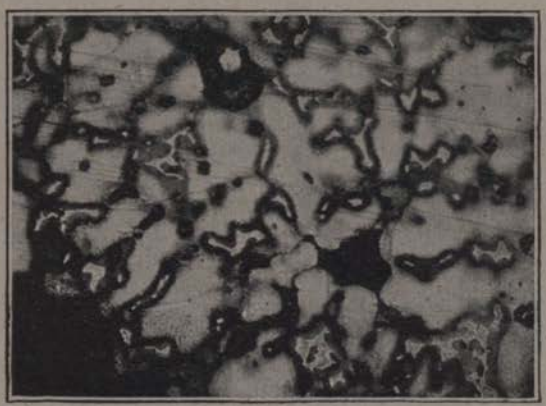


FIG. 164.—Alloy showing progress of solidification. × 100. Copper, 79·9; tin, 9·7; lead, 4·7; iron, 0·3; zinc (α), 5·4. The shaded borders of the α grains (light) indicate variation in composition. The β component (black) contains patches (white) of γ.

elementary metal, *i.e.* well-defined grains similar in character, see p. 10. When solidification extends over a period of falling temperature "coring" may occur, p. 9.

Many alloying metals form more than one solid solution, separating at different temperatures, and may have a dual structure like Fig. 10.

Copper, for example, forms several solid solutions with zinc. The first three are known as α, β, and γ. The alpha range at the point of solidification contains from 100 to 70 per cent. copper; beta, from 70 to 53·5; and gamma, 53·5 to 40. The first series includes the tough, strong alloys, the second are much less tough but useful for casting and other purposes. The third series is extremely brittle. If the cooling of an alloy containing more copper than is required for the gamma series is irregular or chilled it is possible that the solid which first separates may abstract a larger

amount of copper than the average proportion present, and so impoverish the fluid alloy remaining, as to produce some gamma brass and thus render the metal extremely brittle. In some cases it is possible to remedy this by annealing, during which the diffusion of the constituents occurs in the solid state.

The effects produced by controlling the rates of cooling and solidification, *e.g.* by quenching on the one hand or slow cooling in heated moulds on the other, are due to the influence in producing uniformity or otherwise in the composition and structure, and controlling the grain size.

Eutectics result in any alloy when the solidification proceeds in such a manner as to lead to the formation of solid solutions richer than the average in the constituent of higher melting-point, and leave a fluid of lower melting-point which can attain the eutectic composition. Eutectics cannot be formed in any alloys in which the constituents are mutually soluble in all proportions. In binary alloys—two metal alloys—copper manganese and copper nickel may be cited as examples. Eutectics may be formed containing more than two metals. Being the last component to solidify the eutectic occupies an area enclosed by the crystal grains on which it is moulded. In a microscopic section it is usually very irregular in outline and exhibits a striated, herring-bone, or other structure, showing the separation of the components that has taken place.

The effect on the general properties depends on its physical nature and whether it contracts or not on solidifying. When contraction occurs it may produce such porosity as to prevent the alloy being gas tight or even liquid tight. The pores and minute channels formed by the contracting eutectic may (and do in most cases) ramify through the mass in such a manner as to inter-communicate and provide passages.

In some cases the metals are completely insoluble in the solid state, and consequently separate on solidifying, the solid material consisting of the two metals mixed. This occurs with lead and antimony. Antimony or lead separates till the eutectic composition is reached, and then when the eutectic solidifies the metals separate in intimate admixture, producing a laminated or granulated appearance. Eutectics can always be recognised by appearing to be moulded upon the grains, and to act as a filling between them (Fig. 165).

When both metals are more or less soluble in the solid state, the eutectic consists of two saturated solutions, one of each metal in the other. When it solidifies these separate—each being saturated, and produce a result similar to that produced when two metals separate from a eutectic.

Eutectoids may form when changes in solubility occur after complete solidification. The change in solubility of the carbide of iron is noted on p. 180. Similar changes, usually of a less definite and extensive nature, occur in many alloys, separation of the constituents of solid solutions taking place.

Such changes occur in some copper aluminium alloys (90 Al, 10 per cent. Cu).

The production and control of these changes are the objects of the heat treatment to which many alloys are subjected.

Metallic elements like others may form compounds of definite composition with atomic ratios. Such compounds behave as single constituents and may separate, remain in solid solution, or form eutectics and eutectoids like an independent element.

Beside the metals in an alloy, note must be taken of the non-metallic bodies present as impurities or added for specific purposes. Oxygen and sulphur are common impurities, others, like phosphorus and silicon, may be added for specific purposes.

Where they are insoluble or in excess of the solubility they will separate out, segregating round the grains in films or minute globules.

They may have very great influence on the alloy according to the amount and the manner in which they are distributed. See also age hardening, p. 4. Oxides and sulphides are common impurities in most alloys, and methods of melting out of contact of air and furnace gases are designed to minimise troubles arising from this cause.

FIG. 165.—The white body is a eutectic surrounding the crystallites first formed.

Many additions are made to alloys to act as deoxidisers and overcome the difficulties caused by the presence of oxygen. Such additions as phosphorus, silicon, manganese, in small quantities, to brasses and bronzes, and zinc in gun-metal, act principally as deoxidisers. Larger amounts in special alloys have a direct effect in addition to acting as scavengers.

The homogeneity, the properties of the particular components present, and the presence or absence of the eutectic alloy, determine the general physical properties of the alloy and the uses to which it can be put.

Note.—This is only the merest outline of what may occur in the solidification of alloys. Further information must be sought from works on Metallography.

Metals are mixed with each other for the purpose of modifying their properties in order to fit them for special applications. The principal objects are: (1) to harden; (2) to increase the strength, toughness, elasticity, or power of elongation; (3) to facilitate the production of sound and workable castings; (4) to lower the

melting-point; (5) to modify the colour or structure; (6) to resist corrosion.

Thus gold is hardened for coinage and other purposes by the addition of copper and silver and occasionally zinc and other metals. Silver by copper, and so on. Copper is hardened by zinc, and its colour altered to yellow shades, in the various forms of brass. In gun-metal its strength [1] is increased by the addition of tin; its elasticity, strength, and power of elongation by nickel; while addition of zinc, etc., increases the soundness of the castings obtained.

The introduction of zinc and aluminium into copper to produce imitation gold alloys, and of nickel into brass to produce "nickel" silver alloys, are instances of modified colour.

The following list gives the metals in the order in which they affect the colour of the alloy into which they enter, each metal producing a greater effect than that following it:—

1. Tin	4. Manganese	7. Zinc	10. Silver
2. Nickel	5. Iron	8. Lead	11. Gold
3. Aluminium	6. Copper	9. Platinum	

Thus an alloy of 1 part tin and 2 parts copper is white, but nearly 2 parts of zinc must be added to 1 of copper to whiten it. Most metals alloy together when melted, but many have a tendency to separate while cooling. In the production of castings where this tendency is manifested, the alloy should be poured at as low a temperature as possible, while ensuring the filling of the mould and proper admixture of the constituents. The specific gravity of alloys often differs somewhat from that of the mean of the constituents, being sometimes above and sometimes below.

Heat is frequently evolved by the combination of metals. The tendency of metals to alloy with each other varies greatly; thus, copper and zinc alloy well in all proportions; of the copper-tin alloys, those represented by the formulæ Cu_3Sn, Cu_4Sn, Cu_7Sn, are the only ones that show no tendency to liquate.

The purity of the metals employed is of great importance, since minute quantities of impurity frequently exert a marked influence on the properties—0·2 per cent. of bismuth in copper, used for alloying with gold for coinage, destroys the malleability to such an extent as to unfit it for that purpose.[2]

Production of Alloys.—In making alloys, the metals, if not volatile and their fusing-points not too widely apart, may be melted together; but if, as in the case of the copper-tin alloys, one metal is much more readily fusible, it is best added after fusion of the other has been effected.

When one of the metals is volatile, as in the copper-zinc alloys, the volatile metal should be added at as low a temperature as possible after fusion of the copper, in successive portions, each being kept below the surface till melted. In this way it is taken up by the copper as it melts, and is less readily volatilised. The first portions added lower the melting-point, and also cool the mass by absorption of heat in melting. Less loss of zinc occurs in this way. The mixture should be stirred. Oxidation should be prevented during melting by a covering of coke or other carbonaceous body.

Copper-Zinc Alloys.—These are commonly known as brass, but alloys containing tin also are often thus designated. The zinc hardens the copper, causes it to cast sounder, and diminishes the toughness so as to permit of more easy working. The alloys are

[1] In the cast state.

[2] Roberts-Austen, *S. and A. Jour.*, 1888.

strong, and many of them are malleable. Lead diminishes the strength. Brass seldom consists merely of copper and zinc; iron, lead, etc., are often added for special purposes.

TABLE OF COPPER-ZINC ALLOYS

Copper.	Zinc.	Tin.	Iron.	Properties.	Description.
55–60	38–44		1·5–4	Strong as mild steel, highly elastic, less malleable than other alloys.	Aich, Delta, and Sterro metal.
83	17			Softer than most alloys.	Red brass, tenacity 14·5 tons.
72	28			Malleable, ductile; rolls well; bright yellow colour.	Best brass, Bristol sheet.
66·6	33·3			Casts and works well.	Ordinary English brass.
60	40			Rolls well hot; resists corrosion.	Muntz or yellow metal for sheathings.
50	50			Yellow, unsuitable for rolling and drawing.	Common brass and brazing spelter.
66–73	27–34			Yellow, suitable for rolling and wire-drawing; very malleable and ductile.	Pinwire brass.
80–84[1]	15–20			Highly malleable yellow alloys.	Dutch, Bath, or gliding metal. Oreide gold.
75	20–25	0–5		Yellow, malleable; suitable for stamped work.	Mannheim, or Mosaic gold, Similor, Princes metal.
20–47	53–80			Brittle, but will bear slight pressure.	White brass; imitation platinum.
90	10				Gilding metal (Tombac).
85	15				
70	30				Loco tubes. Cartridge cases for drawing purposes.
60	35	1·7	0·5	Pb 1·5. Manganese sometimes present.	Delta metal for extrusion purposes.

Brasses for cold working contain more than 60 per cent. copper. Those for hot working between 60 and 50 per cent.

Silicon-copper-zinc alloys contain from 2 to 6 per cent. silicon, 71 to 95 per cent. copper, and 0 to 27 per cent. zinc. The industrially important alloys contain 2 to 4 per cent. silicon and 10 to 14 per cent. zinc. They have better hot-working qualities than Tombac alloys. Silicon-copper is used for the introduction of silicon.

Many brass alloys contain 0·5 to 2 per cent. of lead and upwards. It is added to many turning alloys to make brass finishing easier.

Nickel to 1 per cent. is added in condenser tubes.

SPECIAL BRASSES

Copper.	Zinc.	Nickel.	Manganese.	Aluminium.	Iron.	Lead.	Description.
56–65	33–40	—	0·8–2	0·25–0·8	0·5 to 1·5	—	Manganese brass (Bronze). Parson's alloy.
90			8		1		Fire-box stays.
56–60	24	14–20	1				Platinoid, sometimes contains tungsten to 1 per cent.
50–58	30–33	12–13		tr	0–1	2·5	Iso. nickel brass for gas and water fittings, etc.
62·78	32·56	Sn 2	0·15–5	0·6	0·92	0·82	Tobin brass (traces of phosphorus).

"Tombac" is a name given to alloys ranging from nearly pure copper to 30 per cent. of zinc.

ENGINEERS' BRASS

This generally contains tin in addition to copper and zinc. Its composition varies from 75 to 90 per cent. copper, 2 to 6 per cent. of tin, and from 2 to 20 per cent. of zinc. It is stronger than ordinary brass, and some of those containing little tin are tougher.

TABLE OF COPPER-TIN ALLOYS

Copper.	Tin.	Zinc.	Lead.	Phosphorus.	Properties.	Description.
90	10				Very tough, finely granular, yellowish-grey fracture, tenacious (18 tons).	Gun metal.
75–80	20–25				Hard, sonorous, brittle, homogeneous, granular.	Bell metal.
95	4	1				Coinage bronze.
82–92	2–6	3–8	0–3			Statuary bronze.
66·6	33·3				Hard, brittle, silver white, conchoidal fracture, takes a high polish, and is used for reflectors, etc.	Speculum metal; zinc, nickel, silver, and arsenic are sometimes added.
88	10	2				Admiralty gun metal.
90	10			0·2		Phosphor bronze for castings.
93	7			0·3		Wire.
87	13			to 1		Bearings.

Copper-Antimony Alloys.—These metals alloy well. The alloy of equal parts of the two metals has a fine violet colour. It is hard,

crystalline, and very brittle, and has no application in the arts. It is known as "Regulus of Venus." Antimony is sometimes mixed with brass to resist action of acids.

Silicon Bronzes.—Various alloys of copper and silicon, containing more or less zinc, iron, and manganese in small quantities, are in use. In the main they resemble bronzes in behaviour. The most important commercial alloy contains 3·5–3·7 per cent. silicon. Silicon bronzes can be forged hot.

The silicon-aluminium-copper alloys and the *silicon*-zinc alloys resemble gun-metal in behaviour.

Tin, Lead, Antimony, and Zinc Alloys.—These comprise the soft solders, type metals, stereotype metals, pewters, etc.

Tin.	Lead.	Zinc.	Anti-mony.	Properties.	Description.
11		1		Very malleable and white.	Spurious silver leaf.
50		50		Casts well, fairly hard.	Pattern alloy.
45	10	45		Casts well and works easily under graver.	For small ornaments.
3	1			Hard and tenacious.	M.P. 198° C.
2	1			Lowest melting-point of series.	Fine solder. M.P. 189° C.
1	1				Tinman's solder. M.P. 205° C.
1	2			Like most others of the series, becomes plastic before solidifying.	Plumber's metal. M.P. 245° C.
		Cu			
60	37		3		Electrician's solder, stronger and harder.
75–94	0–8	1–9	5–7·5	White, rolls and works well.	Britannia metal, for spoons and plate.
	80		20	Expands on cooling.	Type metal.
20	60		20	Lower melting-point. Bismuth often added to lower melting-point.	For small type and stereotype.
5–20	60–80		20–30		General type metal. Linotype.
2·5–3	87–87·5		10		Softer than ordinary type metal, requires watching to maintain composition.
8	77		15		Monotype metal of average quality.

White Metal Alloys

Tin.	Antimony.	Copper.	Lead.	Description.
90	·25	2·5		Original Babbitt metal.
60–80	9–10	1·5–3	6 to 28·5	Babbitt metals. Tin base for heavy loads and high speeds.
40–46	8–9	4·5	40–48	Intermediate for general purposes.
10–20	15	0·5–1·5	65–75	Lead base for medium loads and speeds and light high speed.
5	15		80	Magnolia metal.
8·25	17		74·5	Posts zero metal.

ZINC "DIE CASTING" ALLOYS

Zinc.	Aluminium.	Copper.	Magnesium.	Description.
78–93	4–22	0–3	0–1	For die casting. Important that volume shall remain constant. May be aged. Same as Tyseley alloy.
87·28	7·1	0·5	0·42	Fe, Sn, and Si traces (good).

FUSIBLE METALS AND ALLOYS

Tin, Lead, Bismuth Alloys, used for fusible plugs and "quick" solders for pewter, etc.

Tin.	Lead.	Bismuth.	Cadmium.	Melting-point.	Description.
20	30	50		197° F.	For fusible plugs, taking impressions of dies, etc. Expands on cooling.
12·5	25	50	12·5	150° F.	
58·8	29·4	11·8			Pewterer's solder has a lower melting-point than work to be soldered.
15·5	30·8	38	15·5	160° F.	Woods' alloy, M.P. 71° C.
25	25	50			Rose's alloy.

GOLD, SILVER, AND PLATINUM ALLOYS

Gold.	Silver.	Platinum.	Copper.	Zinc.	Description.
	92·5		7·5		English standard silver.
	90		10		French and German coinage.
	75		25		German silver plate.
	91·66		8·34	–	Indian rupee, Brazilian coinage.
	94·5		5·5		Netherlands coinage.
	66·6		22·2	11·1	Silver solder.
91·66			8·33		British, Turkish, Brazilian gold coin.
98·9			1·1		Hungarian ducat.
90			10		German, French, Italian, Belgian, Spanish, United States, Swiss, and Russian gold coins.
10	. 6		4		Gold solder.
	65–83	17–35			Dental alloys.

Aluminium Bronze.—The proportion of aluminium alloyed with the copper varies from 1 to 10 per cent. The alloys are as strong as mild steel, highly malleable, elastic and ductile. The presence of other metals impairs the quality. An alloy containing 10 per cent. has a tensile strength of 40 to 45 tons per square inch.

Manganese Bronzes contain copper, manganese, aluminium, zinc, iron, and tin. Sometimes they are characterised by hardness, elasticity and strength combined with toughness and resistance to corrosion. They can be rolled and forged and pressed hot. An important application is for the propellers of steamships. They are also used for general engineering brass work. The manganese is generally introduced in the form of ferro-manganese or as manganese copper.

Phosphor Bronze is a bronze containing a small proportion of phosphorus, introduced either as phosphor tin (obtained by dissolving phosphorus in molten tin), or phosphor copper (containing up to 20 per cent. of phosphorus), after fusion of the ordinary ingredients. The tin varies from 4 to 10 per cent., and the phosphorus from 0·1 to 1. Where toughness and ductility are required, the phosphorus should not exceed 0·1. Metals containing more increase in hardness and are used for valves, bushes, cog-wheels, etc. It should be cast at as low a temperature as possible.

The beneficial effects of phosphorus and silicon are generally attributed to the powerful deoxidising influence they exert on account of their affinity for oxygen.

Nickel Bronzes.—The introduction of nickel into brass and bronze alloys has become common. Its action in raising the tensile strength, elasticity, hardness and resistance to erosion and heat effects has led to very general adoption.

NICKEL ALLOYS

Nickel.	Copper.	Zinc.	Iron.	Lead.	Tin.	
14–31·5	40–56	23–26	2·5–3·5		0·5	Arguizoid, Chinese white copper.
15	60	25				Common German silver.
21	56	23				Medium " "
25	50	25				Good " "
28	38	33				Best " "
20	80					Cupro nickel, used for bullet casings, draws well. All white, tough, malleable; for rolling a little lead is often added.
12–13	50–58	30–33	0–1	2·5		Iso nickel brass, white, hard, resistant; casts and machines well. Gas and water fittings.
60–67	28–33					Monel metal, contains manganese up to 2·5 per cent. and iron 2. Manufactured metal may contain a little aluminium or magnesium.
50						Coinage silver with 50 per cent. silver requires care in manipulation.
14–20	56–60	24				Platinoid. The alloy sometimes contains tungsten to 1 per cent.

SPECIAL NICKEL ALLOYS

Hypernik is a special alloy containing 50 per cent. nickel used in transformers.

Permalloys contain up to 78 per cent. nickel. Mu metal contains 76 per cent. nickel, 17 per cent. iron, 5 per cent. copper, and 2 per cent. manganese and chromium.

Kanthal alloys for wire for electric fires and similar purposes contain chromium, cobalt, and aluminium.

	Nickel.	Chromium.	Manganese.	Iron.	
Nichrome .	60	12	2	26	Chemically resistant, resists oxidation at red heat; used for resistance heating.
Chromel . .	80	20			
Incomel . .	80	12–14		6–8	Hard, elastic, chemically resistant.

	Nickel.	Copper.	Manganese.	Zinc.	
Nickeline . .	15	60		25	
Constantan .	40–55	45–60			Used in electrical resistances, low temperature coefficient.
Eureka . .					
Manganin .	2–16	50–85	10		
Monel metal .	67	28			Chemically resistant, strong.

	Nickel.	Copper.	Chromium.	Molybdenum.	
Illium [1] . .	61	6	21	5	Strong, resistant. Calorimeter bombs.
				Tungsten.	
Nickel tungsten alloy	82–90			10–18	Acid-resisting alloy.

ALUMINIUM ALLOYS

Aluminium.	Copper.	Zinc.	Magnesium.	Nickel.	
80–98	1·5–15	0–14·5	0–1·7	0–1	Casting alloys for various purposes.
80–82	4·5–6	12·5–14·5			Si 0·5–1. Piston alloys.
88	12				Piston alloys.
	8				For general castings, "No. 12" alloy. Maximum tensile strength.
	6–8				2L11 alloy.
	11–13				2L8
	2·5–3	12·5–14·5			2L5. Extensively employed for gear boxes, crank cases, and other parts, loses strength when hot.
	3·5–4·5		1·2–1·7	1·8–2·5	L24. Y alloy for castings and forgings. Heat treated up to 22 tons tensile, connecting rods and highly stressed parts.
				(Mn)	
	3·5–4·5		0·4–0·7	0·4–0·7	2L3. Duralumin. Iron not to exceed 0·75 for forging, rolling, hot stamping, heat treated and aged up to 26 tons tensile.
	2–2·5	4·5–5			2L32. Alloy bar.
	2	2	0·5–10		Magnalium.
	10		10		Duralum.

Hiduminium contains aluminium with Cu 1·5–2·5, Ni 0·5–2, Mg 1·4–1·8, Fe 1·2–1·5, Ti 0·02–0·12, Si 2·0.

The balance where not stated is aluminium and normal impurities. Fe is generally below 1 per cent., but occasionally up to 1·5. Most

[1] Iron, aluminium, tungsten, and manganese make up the remainder.

aluminium alloys contain silicon or magnesium or both. The amounts, unless specially introduced, are below 0·5. Silicon may be introduced by melting in contact with siliceous materials.

Copper increases tensile strength, maximum being reached at 8 per cent. Zinc reduces ductility and makes alloy hot short.

ALUMINIUM SILICON ALLOYS

Aluminium.	Silicon.	Description.
85–89	8–15	Casting alloys. Alpax. Wilmill.
88–89	11–12	Silumin. All silicon aluminium alloys may contain iron and magnesium.

Alloys with silicon from 5 to 13 per cent. silicon are said to shrink less and be stronger than other alloys.

MAGNESIUM LIGHT ALLOYS

Aluminium.	Magnesium.	Silicon.	Iron, Calcium and Alkalies.	
69·55	29·54	0·18	0·73	Strong and light.
90·	10·			Alumag.

DENTAL ALLOYS

Platinum . . .	17 to 35 per cent.	Require much skill in making to secure proper admixture.
Silver	83 to 65 „ „	

DENTAL AMALGAMS

Amalgams of tin and mercury, and mercury with cadmium, are employed for filling teeth. These amalgams become plastic by pounding or kneading when slightly warmed, as in the hand, but set hard without contraction. A copper amalgam was formerly much employed, but it requires stronger heat to make it plastic.

Tin amalgam is made by grinding 1 part of tin with 4 of mercury and squeezing out the excess mercury in chamois leather. The soft residue hardens in a few days.

Tin cadmium amalgam is made by melting 2 parts of tin with 1 part of cadmium, and adding an excess of mercury. The excess is removed as before, after well grinding in a mortar.

An amalgam of tin, silver, and gold is used as a cement for teeth: 1 part of gold, 1 tin, 3 silver are melted together. The alloy is pulverised *while hot*, an equal weight of mercury added, and thoroughly kneaded together.

A dental amalgam containing a minimum of 65 Ag, 25 Sn, with a maximum of 6 Cu and 2 Zn is coming into use.

Other dental alloys replacing the 50 per cent. Pd, 50 Ag + Au alloy, range from 10 to 20 Au, 27–50 per cent. Ag, 21–30 per cent. Pd, 10–20 per cent. Cu, 1–5 per cent. Zn. Some contain indium. Gold alloys containing from 78 to 83 Au and 3–15 per cent. Ag are employed.

Sodium amalgam is produced by adding sodium to mercury; the combination causes great evolution of heat. It is prepared in considerable quantities for export. For this purpose it is packed in lime, to prevent access of moisture or carbon dioxide, in metal-lined cases. The amalgam contains about 3 per cent. of sodium, and is tolerably hard and semi-crystalline.

Iron Alloys

Nickel.—About half the nickel produced is now used in alloy with iron in nickel steels, either alone or associated with other elements. Straight nickel steels contain from 1·5–5 per cent. The great bulk, containing from 2–4 per cent., is used in general engineering work, large bridge work, dynamo, automobile, gun, and marine forgings, engine and machine work. Properly heat treated it has a high elastic limit and is tough. Nickel cast irons contain from 1–5 per cent.

High nickel alloys over 20 per cent. resist corrosion. Steels containing 24–25 per cent. are non-magnetic and expand little by heat. Invar metal, containing 35–38 per cent. nickel and low carbon (0·1–0·15), is used for balance wheels, measures, and instruments where precise measurement is essential. Its coefficient of expansion at ordinary temperatures is negligible. Platinite, with 46 per cent. nickel and 0·15 carbon, has the same coefficient of expansion as glass.

The wire used for sealing in the filaments in electric light bulbs contains 38 per cent. nickel and is coppered. The expansion can be made to suit the glass of the bulb.

The behaviour of nickel steels is seriously influenced by the amount of carbon present, especially the magnetic and volume changes.

Iron and Zinc.—Iron dissolves in zinc, heated to nearly its boiling-point to a considerable extent. The iron in delta metal and other copper alloys is introduced by saturating molten zinc with iron, and adding this alloy to the copper in sufficient amount. A hard alloy of zinc and iron forms in galvanising pots, and zinc melted in iron vessels takes up iron.

Chromium.—The amount of this element added to steel varies from 0·25–18 per cent. for various purposes. The metal, even in small quantities, increases the tenacity and hardness. It retards the transition of the carbide to pearlite by lowering the critical point. It reduces grain size, and thus increases tenacity and wearing qualities, and raises the yield point without diminishing toughness. It is usually employed in conjunction with nickel and vanadium or molybdenum. It promotes the penetration of carbon in case-hardening steels. Chromium cast irons contain from 0·1–1 per cent.

High chrome steels are resistant to corrosion. Alloys containing 7–8 per cent., used for malleablising pots, do not scale readily on heating and the scale is adherent. Rustless iron contains 12 per cent. chromium and 0·1 carbon. The effect of carbon in raising the hardness is very rapid.

Rustless steel contains from 12–18 per cent. chromium and not more than 0·3 carbon. Silicon to 0·2 per cent. may be present.

Nickel Chrome Rustless Steels contain from 6–12 per cent. nickel, 18–23 per cent. chromium with 0·1–0·3 carbon. The resistance to corrosion is affected by the structure of the metal. It is greatest in the austenitic condition.

Chromium is introduced into the metal for shell cases and armour, and in "high-speed" steel. Structural steels used in automobile work contain up to 1·5 per cent.

Tungsten Steel.—All self-hardening—air-hardening—tool steels contain tungsten in amounts varying up to 18 per cent., usually below 9. It is generally associated with chromium, vanadium, and molybdenum. Tungsten alloys are very fine grained, hard, break with an almost conchoidal fracture and require care in forging. Mushet steel containing 4–9 per cent. of tungsten was the forerunner of the air-hardening steels.

Manganese (Hadfield's) Steel.—Although with more than 2½ per cent., manganese, iron manganese alloys are weaker and with larger amounts brittle, when manganese is present beyond 7 per cent. the embrittlement of iron caused by its presence disappears. With 12–13 per cent. great hardness and toughness is developed. It is toughened by quenching in water from 1000° C. and becomes ductile and tough. The alloy is practically unmachinable. It hardens under pressure and is used for jaw crushers, switches, and railway crossings, etc.

Molybdenum is now alloyed in steels to develop its shock-resisting qualities up to 2 per cent. It is more effective than vanadium.

Stellite consists of 60 per cent. cobalt, 22 per cent. molybdenum, 11 per cent. chromium, 3 per cent. iron, 2 per cent. manganese.

Vanadium is present in quantities varying from 0·1–0·5 per cent. It increases the toughness and reliability, and in high-speed steels furnishes a means of controlling the heat treatment. It is used in conjunction with chromium for springs, constructional work, tools and forgings. **Cobalt** is used in stellite (see above) and in magnet steels, see p. 329.

Vibrac is a nickel-chrome molybdenum steel with a very high yield point.

Armco is a nearly pure iron containing under 0·1 per cent. total impurity.

"Harveyised" armour plates are nickel-steel plates, case hardened on the surface by heating in contact with charcoal, after the manner of making blister steel.

Hardening and Tempering (secondary hardening) High-Speed Alloy Steels.—Modern high-speed steels are forged at 1000° to 1100° C., heated to 1380° to 1400° C. in special furnaces, withdrawn, and cooled in a blast of cold air or sometimes in oil. Tempering or secondary hardening consists of reheating the steel to about 550° to 600° C. for a few minutes and cooling in air or quenching in oil. This heat treatment requires great care and special furnaces and appliances are necessary. Pyrometers are employed to control temperatures. The first heating must reach the required temperature but not burn. In secondary hardening the temperature must not much exceed that required by more than 20 or 30° C., or the hardness will be much reduced.

PYROMETRY

The measurement of moderate temperatures is rendered easy by thermometers of various types. It is much more difficult to measure high temperatures and rapid fluctuations of temperatures.

For metallurgical purposes it is necessary both to measure high and also small and rapid changes at those temperatures.

Scientific control of most metallurgical operations, especially those connected with the working and heat treatment of metals, is based on the physical changes taking place at fixed temperatures or existing above or between certain limits of temperature. To ensure this condition accurate control of temperature is necessary.

In annealing, wire drawing, steel hardening, and tempering, malleableising iron, case hardening, general heat treatment, age hardening, in fact in all modern metallurgical improvements and developments, pyrometers must be employed, and in many cases permanently installed, to ensure success of the operation. Many of the latter are connected with permanent self-recording appliances to both check the process and furnish evidence of the conditions having been maintained (some give warning when conditions are not satisfactory), pyrometers being installed at various points to ensure uniformity of heating.

Almost every physical change which substances can undergo when heated has been exploited in the construction of instruments for measuring temperature. Among these may be mentioned: specific heat; change of state; conductivity; changes in electrical resistance; heat radiation and absorption; thermo-electric effects; and photometric intensity. These have been applied in many ways. Preference is given to those phenomena that show (1) constant and regular variation over wide ranges of temperature; (2) ease of observation and accurate determination; (3) independence of the personal factor of the observer; (4) simplicity of securing an automatic record.

Among the many instruments and methods in use may be noted the following:

Resistance Pyrometer.—The Resistance type of instrument operates by indicating the change in electrical resistance of a conductor placed in the hot region.

Note.—The resistance of metallic conductors increases with the temperature.

A coil of fine platinum wire wound on a mica frame (or other insulating support) is enclosed in a silica tube protected by a sheath of iron. The ends of this coil are connected by leads with binding screws on the cap. False leads extending to the points of connection of the platinum coil also connect with separate terminals on the tube cap.

The increase in resistance of the heated coil is measured by making it and its leads one arm of a Wheatstone bridge. The false leads are

connected in the compensating arm of the bridge, and the increase of resistance measured, in the usual manner, by adding resistance in that arm till zero is reached.

At temperatures above the boiling-point of sulphur (444° F.) the increase in the resistance of the platinum is not proportional to the increase in temperature. It therefore becomes necessary to determine and apply the correct factor for the instrument if the calibration has not been carried beyond that temperature. This varies with the purity of the platinum and alloy. For practical purposes a direct reading scale, sometimes called a "fixed point" scale, can be established by calibration, using the melting-points of metals to determine the points. See pp. 353, 356.

Thermo-electric Pyrometers.—Thermo-couples. Professor Seebeck of Berlin, in 1821, discovered that if one of the junctions of a closed circuit consisting of two metals be heated a current was generated. This laid the basis of thermo-electricity, and Becquerel found that the current was proportional to the difference in temperature.

TABLE OF ELEMENTS IN ORDER OF THERMO-ACTIVITY

Bismuth	+25	Gas coke	−0·1
Cobalt	9	Zinc	0·2
Nickel	5	Cadmium	0·3
Lead	1·03	Arsenic	3·8
Tin	1	Iron	5·2
Copper	1	Antimony	9·8
Platinum	0·7	Tellurium	179·0
Silver	1	Selenium	−290

Mathieson's table of relative activity is shown above.

In the figures given the copper-silver couple is taken as unity. A bismuth-nickel couple would give a value 20 (25−5), a bismuth-antimony couple 34·8 (25+9·8). This is about equal to 1 volt.

A thermo-couple, used as a pyrometer, consists of rods or wires of the two selected metals, securely joined together at one end. The other ends are connected with apparatus for detecting and measuring the electrical disturbance set up when the junction is heated. The free ends must remain at a constant temperature—the cold junction. Sensitive "dead beat" galvanometers are employed for detecting, and even indicating in some cases, the temperatures of the hot junction. In other cases varying resistances (Wheatstone bridge type) or means of producing an opposing E.M.F. (potentiometer type) are used to determine the temperature by zero methods. The latter are the more accurate methods.

In the application of the principle to pyrometry, metals of high melting-point must be selected, and for high temperatures those giving comparatively low E.M.F. (voltage) to enable accurate measurement to be made by means of sensitive instruments.

Metals and alloys of lower melting point may be used in radiation pyrometers.

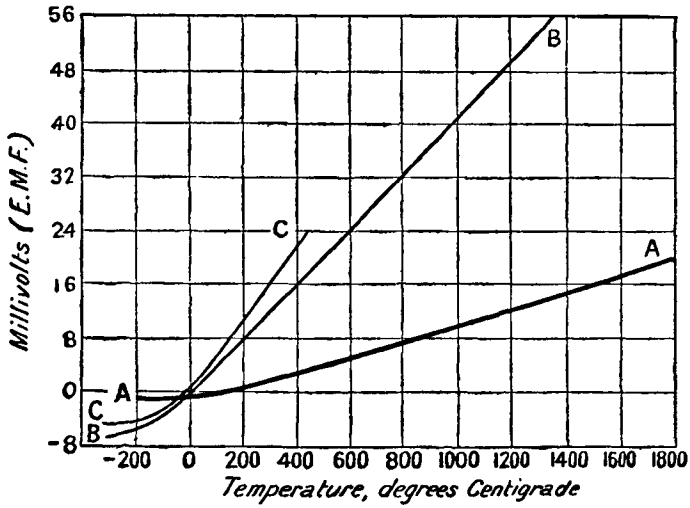
The couples commonly employed may be divided broadly into two classes, (*a*) base metal couples, and (*b*) platinum-platino alloy couples.

Base metal (nickel, iron, nichrome, etc.), couples can be made up in much more robust forms than platino couples, and cover a considerable range of temperatures.

The couples commonly employed are—

Platinum v. Platinum + 10 per cent. Rhodium.	Copper v. Constantan.
Platinum v. Platinum + 10 per cent. Iridium.	Iron v. Constantan.
Chromel v. Alumel.	Iron v. Nickel.
Chromel v. Nickel.	

Fig. 166 shows the E.M.F. in millivolts at different temperatures for copper constantan, chromel alumel, and platinum platino-rhodium couples.[1]



Adams, Trans. A.I.M.E., 1920.]

FIG. 166.—A, Platinum—Platino-Rhodium Couple; B, Chromel—Alumel Couple; C, Copper—Constantan Couple.

It will be observed that in the lower ranges of temperature the increase in E.M.F. is not proportional to the rise in temperature. It becomes so at higher temperatures and the curve is a straight line. The platinum combinations are less affected than the base metal in this respect.

Thermo-couples like thermometers are calibrated by exposure to known fixed temperatures. The points commonly selected are the melting-points of pure metals or eutectics to ensure sharp indications of freezing by prolonged arrests of cooling.

[1] L. H. Adams, Trans. A.I.M.E., 1920.

TABLE OF CALIBRATION TEMPERATURES

Tin freezing-point	231·8° C.	Antimony	632° C.
Lead	327·4°	Common salt	801°
Zinc	419·4°	Silver	961°
Aluminium-copper eutectic	542°	Copper	1083·5°

Boiling sulphur at 444·5° is often employed.
Fused metals must be covered with charcoal and stirred while solidifying.

The diagram shows the voltages of the couples included. The voltages of other couples are as follows :

E.M.F. OF OTHER COUPLES [1]

T°	Iron-constantan. E.M.F. (millivolts).	Titan alloys. E.M.F. (millivolts).
0	0	0
200	10·8	8·27 [2]
400	22·2	16·46
600	33·4	24·97
800	45·8	33·25
1000	58·6	41·27
1200		48·83
1400		56·12

The couples for immersion are protected in porcelain, silica or other refractory tube.

Since the E.M.F. generated is independent of mass the couples may be made of wire or rods or tubes—in the case of base metal couples—with equal efficiency.

Notes.—Chromel is an alloy of 80 per cent. Ni, 20 per cent. Cr.; Alumel of 94 per cent. nickel, 2 per cent. aluminium, 1 per cent. silicon, 2·5 Mn. Freedom from impurities is important—in the one case iron and the other *excess* silicon. The combination will stand up to 1000 or 1100° C., and for short periods to higher temperatures (1300° C.). Constantan or "eureka" is an alloy of 60 per cent. copper, 40 per cent. nickel, traces of manganese. Great uniformity in quality can be attained. The satisfactory use of iron as a thermo-electric element depends on its uniformity in composition and physical character. It is generally unreliable above 800° C.

Owing to a transformation in nickel it is not reliable below 400°, but may be used to 800° C.

In making thermo-couples the hot junction should be welded or fused, or in some cases soldered (brazed). Twisting wires together in such a manner that they will not work loose is difficult.

Wire couples will need careful protection in tubes, but "pokers" and similar robust forms may be unprotected.

The "cold junction," *i.e.* the free ends of the elements are connected with the indicator employed. They must be kept at constant temperature for accurate indications and in experimental work are ice cooled.

[1] By courtesy of the Cambridge Scientific Instrument Co.
[2] Test made at N.P.L.

The ends placed in a vacuum flask in a sheltered spot will generally suffice for practical purposes if the calibration be carried out under similar conditions.

The lengths of lead are unimportant if the resistance of the leads is infinitesimal or nil. It is better to employ standard leads with which the calibration is carried out.

The indicating instrument most commonly used is a moving coil galvanometer. Owing to the uniformity, permanence, and strength of the magnetic field in which it moves, and the weak effect of the coil compared with that of the permanent magnets establishing the field,

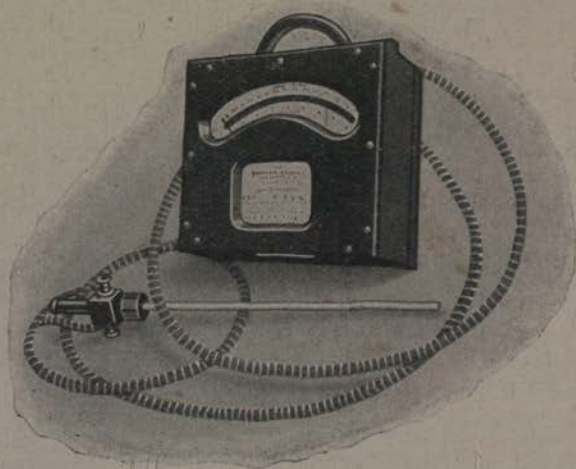


FIG. 167.—Showing couple and connection, poker and wire couple.

its movements are definite in direction and free from oscillation, making it a "dead beat" instrument, the readings of which can be immediately taken or recorded as desired.

The coil may be suspended or work on a suitable pivoted arrangement—the latter form being portable and little less sensitive.

Very sensitive instruments are necessary, as in direct-reading instruments the full scale may only represent 10 millivolts.

The pointer—carried by the coil—moves over a quadrant scale as shown in Fig. 167.

With a high-resistance circuit small variations in total resistance produce no effect, but in some cases with base metal couples the total resistance of the circuit is very low and heavy couples and connections are necessary as well as provision against possible changes.

Records are obtained by the "thread recorder" or by ink pencil on moving charts.

In the "**thread recorder**" (Fig. 168) the chart is carried on a time-driven horizontal rotating cylinder. Across the top, parallel with the axis of the cylinder, passes an inked thread, above which the pointer moves between the thread and a chopper bar which at fixed intervals is depressed, forcing the pointer down on the thread to mark the paper beneath.

In other recording instruments, such as the Callender, Leeds and Northrop and others, electrical or mechanical means are provided by which at stated intervals the position of the needle is recorded and simultaneously the necessary adjustment made to restore balance. An inked pen traces the movements on a chart. In many cases several pyrometers may be put in connection with the same recorder, records of each circuit being made in turn at fixed intervals, all the movements of contacts and adjustments being made by mechanical means automatically.

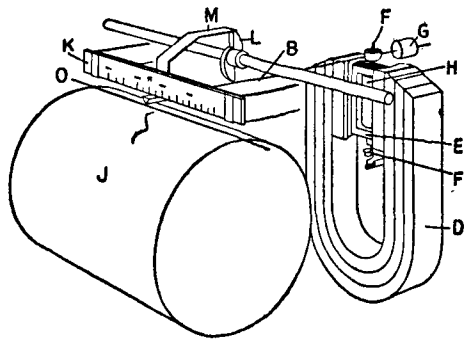


FIG. 168.—Thread recorder. The galvanometer needle, B, has a wedge-shaped end and is carried by the swinging coil, E, which is suspended and connected with the pyrometer at FF. The coil moves round an iron armature, H, which equalises the magnetic field covered by the moving coil. A small balance-weight, G, is provided to maintain balance. D is a powerful permanent magnet. The chart is carried by the time-driven drum, J, over which passes the inked thread, O, just out of contact with the chart. At definite intervals the chopper bar, K, is depressed by the cam, L, acting through the lever, M, causing the needle momentarily to press the thread into contact with the paper, making a mark, thus producing a series of dots, at timed intervals, forming a curve. Immediately a mark is made the bar is lifted and the needle swings freely.

In the above examples, and in many others, the indicating galvanometer is of such construction and has such a resistance compared with the other parts of the circuit that the movements of the pointer over the scale may be used directly, within certain limits, as showing the temperature, the galvanometer scale having been calibrated by reference to melting-points or other means.

For most practical purposes no appreciable error is introduced, but for purposes where greater accuracy is necessary "Zero" methods are employed. In these methods the pointer is brought back to zero for each determination by (1) varying the "resistance" in the circuit or (2) by balancing the potential difference created, by an equal and opposite potential.

The amount of resistance so introduced or the potential required to

produce balance and bring the pointer back to zero can be measured and indicated with great accuracy and furnishes means of determining the temperature.

Such means are applied to various forms of pyrometer, including Thermal junction and Resistance pyrometers.

Note.—The principle of the Wheatstone bridge used in all methods of measuring resistance is illustrated in Fig. 169. Its operation depends on:

(1) that when equipotential points are connected by a conductor no current flows.

(2) the fall in potential in a conductor is in an inverse ratio to the resistance.

(3) that in a divided—by-pass—circuit the potential at the two junctions is the same in each circuit.

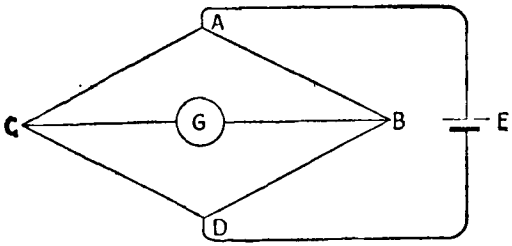


FIG. 169.

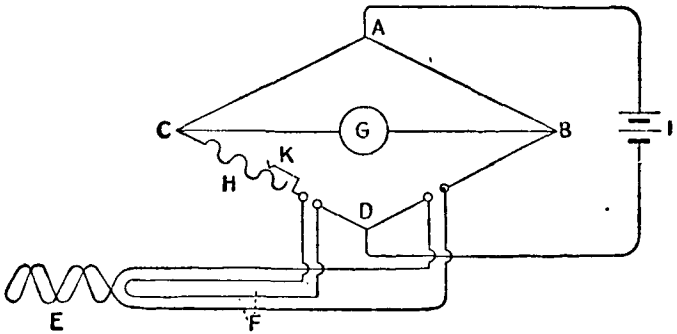


FIG. 170.—Showing connections of a "bridge" indicator. E, platinum coil and leads; F, compensating duplicate leads; H, variable resistance; K, sliding contact.

It follows that in the circuits ABD, ACD, the current supplied by the battery E will divide at A in proportion to the resistances in the two circuits. A and D are at the same potential for both circuits. If each of the circuits is of uniform resistance throughout its length the middle points of each, no matter what their individual resistance, will be at the same potential. If a galvanometer be connected up with these points no current will flow. Similarly at any proportional points, $\frac{1}{3}$, $\frac{1}{4}$, or other proportion, the galvanometer will show no current.

If, therefore, the proportions in one circuit be known and a point be searched for in the other at which no current passes when connection is made, it follows that the selected point has the same relative position in the other circuit.

If, therefore, a ratio be arbitrarily selected in one circuit, say AB : BD :: 1 : 3, an unknown resistance can be measured in the other circuit by making it one of

the branches, say AC, and introducing *known* resistance in the other, CD, until no current passes, showing that equipotential points have been established. The ratios thus establish the actual resistance of the *unknown*, the ratio AC : CD must be 1 : 3, and CD is known.

In the measuring instruments employed the ratios are pre-established. The branch CD may receive the duplicate dummy compensating leads [1] and the branch BD, the pyrometer leads. CD also contains in circuit a resistance, variable at will, which can be varied as T° rises to restore balance. A coil of wire with movable contact may be used for this purpose, and the *increased length of wire* necessary to produce equilibrium may be divided into equal divisions like a thermometer scale. This gives the platinum scale. It can also be calibrated by reference to known fixed temperatures.

In the explanation just given the difference of potential remains constant—that of the battery in circuit. But the method of balancing may be also applied to potential differences such as those set up in thermo-electric circuits. In this case balance by adjustment of the resistance may be made, but it is necessary to have a constant electrical potential for reference purposes and a "standard" cell must be used for calibration purposes.

When this is done and potential differences are measured the instrument becomes a potentiometer. The diagram Fig. 171 illustrates the principle. APB is a closed circuit in which the battery P maintains the points of the conductor's resistance AB at a constant difference of potential—that of the battery itself. G is a very sensitive galvanometer, mirror or other form, one terminal of which is permanently connected with B. The other terminal of the galvanometer is connected with one end (conducting lead) of the source of variable potential—say a thermo-couple T in opposing phase to the battery. The other lead of the thermo-couple forms a movable contact with the wire AB.

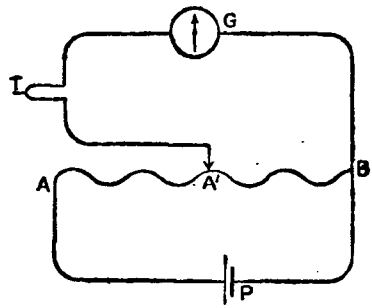


FIG. 171—T, thermo-couple; G, galvanometer; AB, variable resistance circuit; A^1, sliding contact; P, battery at constant voltage.

The system is balanced in the unheated state by adjustment to a position where the galvanometer shows no deflection. The difference in potential which occurs when the junction is heated will cause a deflection, but by moving the sliding contact along AB an equal and opposite change in potential may be introduced and the galvanometer brought back to zero. Since the potential falls uniformly in AB from A to B, the potential thus introduced will be represented by the proportionate length of the conductor (resistance) introduced, and if the E.M.F. of the battery be known, the actual rise in potential at the hot junction may be expressed in millivolts, *e.g.* if the final contact is

[1] To eliminate any error due to the leads becoming heated.

the middle point of AB, the potential difference caused by heating T is half that of the battery.

In actual work, if the difference in potential (voltage) of the battery be maintained constant all readings will be comparative and the instrument may be calibrated. It can be checked from time to time by a standard (Clark's) cell.

This is the most accurate method of determination, and various appliances embodying the principle, many of which are very complicated, are employed for research purposes and in practice.

For practical purposes the necessary apparatus can be put into a portable form, but a very sensitive galvanometer of portable type replaces the mirror galvanometer.

In most cases, however, sensitive direct-reading millivoltmeters are employed for works and other purposes, direct readings and not zero readings being taken. They are calibrated for temperature.

Radiation Pyrometers.—In radiation pyrometers the heat-light rays radiated from the objects or furnace are used to indicate the temperature.

The simplest instrument is one in which a direct observation is made through a red glass screen. A long wedge of red glass of small angle is moved till the light passing through the window just disappears, and from the position of the wedge—the thickness of glass interposed—the temperature is read. Such a method, although useful, depends too much on the personal factor.

For practical purposes two types of radiation pyrometer are in common use. In the simpler form the heat-light from the source passing through an aperture falls on the surface of a concave mirror—gold or stainless steel to preserve brilliance—and is focused by it on a minute thermo-couple which is placed at the focus of the mirror. Since the actual rise in temperature is small (never exceeding 80° C. in any form) the most sensitive elements giving the highest E.M.F. may be employed, giving an open scale.

The Fery pyrometer is shown in Figs. 172 and 173. The heat-light entering the telescope is focused on a very small thermo-couple N by the concave mirror C, adjustment of which can be made by the rack and pinion F. The path of the rays is as indicated. Focusing is done by the eye-piece E sighting through a central opening in the mirror C. The thermal junction is placed in an opening in a small divided mirror consisting of two semicircular wedges. When in perfect focus the two parts of the image are in perfect alignment (*b*, Fig. 173). If not in focus they appear as *a* or *c*.

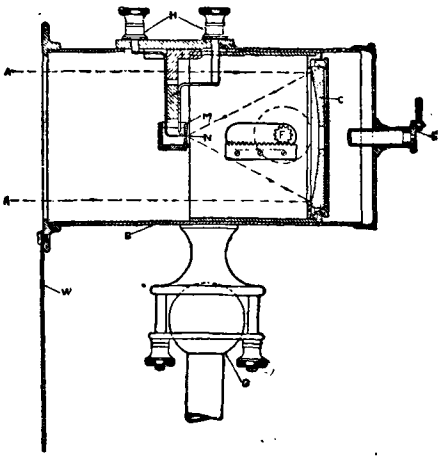
The thermo-couple is connected through the terminals H with an indicating or recording galvanometer calibrated to give direct temperature readings when used with standard connecting leads.

The mirror C, formerly gold faced, is now made of rustless steel, which can be polished without scratching and so preserve its brilliance.

Distance from the object may vary within wide limits, but the body sighted on should have a diameter (size) equal to 1 inch for every

2 feet distance of the telescope from the object to ensure that the image will overlap on all sides of the thermo element in the telescope.

In the Foster fixed focus instrument the aperture at the end of the tube and the thermal junction are at conjugate foci, so that a hot object put in contact with the end of the tube would be in focus, and radiating heat would be automatically brought to a correct focus. Within wide limits the distance of the source of heat from the mirror is immaterial so long as the cone of heat-light rays from the source of heat fills the aperture, and thus fulfils the requirements of "black body" radiation. (Fig. 174.)

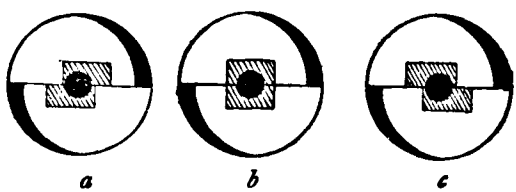


Courtesy of the Cambridge Instrument Co.

FIG. 172.—Fery pyrometer. Telescope, etc.

The inside of a furnace or other closed space which is fairly uniformly heated, such as a long tube, is practically a "black body." Objects inside uniformly heated and sighted through an aperture fulfil the conditions, but an outside object exposed to the air, especially if it has reflecting power, will depart widely.

Total radiation pyrometers are generally standardised to "black body" conditions (see footnote). When used under other conditions, as, for example, to take the temperature of external objects such as



a *b* *c*

Courtesy of the Cambridge Instrument Co.]

FIG. 173.—Shapes of aperture.

the surface of molten metals or slag, the temperature recorded depends on the radiating power—emissivity—of the material.

The temperature registered by the instrument, compared with the actual temperature as found by separate determination by a thermal junction furnishes data for correction for that substance as the emissivity varies little at temperatures above redness. This correction is often very large, especially for molten metal surfaces.

Thus iron at 1500° C. may indicate only 1000° and at 1685° only 1153°.

Note. The Stefan Boltzman law on which radiation pyrometers are based states that the total heat radiation from a black body is proportional to the fourth power of the *absolute* temperature. It applies only to black bodies, a black body being one capable of absorbing all the heat received without reflection from the surface or conduction into the interior of the mass.

Photometric Pyrometers.—Other instruments like the Wanner type pyrometer—probably the best of the radiation instruments—use selected rays. Complicated optical arrangements are employed to select and polarise a particular red ray from the spectrum of the light emitted by the furnace. The intensity of this is compared photometrically with the light from a standardised electric lamp contained in the instrument, the brightness of which is kept constant. The comparison resembles that of a polarimeter. There is some personal error, but with care and experience excellent results are obtained.

The **disappearing filament pyrometer** has come rapidly into favour on account of its accuracy, simplicity, and portability.

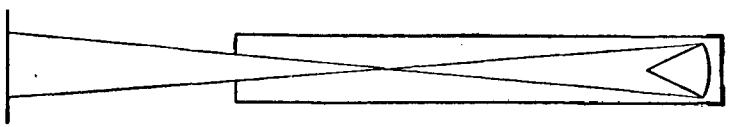


FIG. 174.

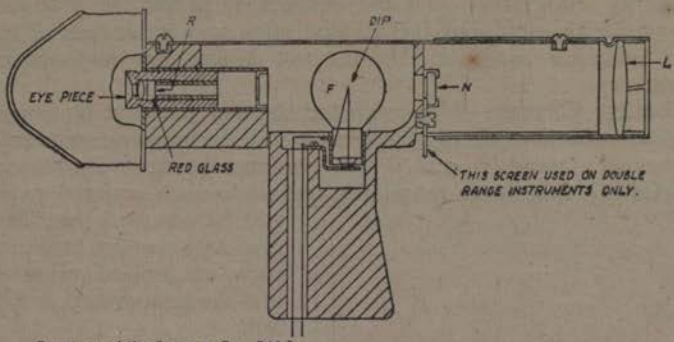
In instruments of this class the heat-light from the furnace is focused in the plane occupied by the tungsten filament of an electric lamp, the tip of which occupies the field of view. It is thus seen on a background formed by the source of heat on which the instrument is focused. The current supply to the filament is under control, and can be adjusted to increase or diminish its brightness at will. When the filament glows with the same intensity as the background, the filament disappears from the field of view. The slightest variation in either direction makes it visible.

The calibration of such an instrument therefore becomes easy, the current being altered by varying the resistance or the E.M.F., and measuring the total required to obscure the filament.

Figs. 175 and 176 show such a pyrometer and its connections. With the instrument as shown temperatures up to 1350° C. may be observed, but with a screen inserted it may be used for higher temperatures. It must, however, be separately calibrated *with* the screen. The two scales overlap. The indicating apparatus consists of a milliammeter and variable resistance, and to ensure accuracy both lamp and instrument must be checked from time to time.

Black body conditions are necessary for accuracy. Furnace interiors and the like fulfil these, but for surface readings precautions similar to total radiation pyrometers must be observed.

In many cases in practice—such as forging temperatures—it is only necessary to accurately repeat conditions, and once having estab-



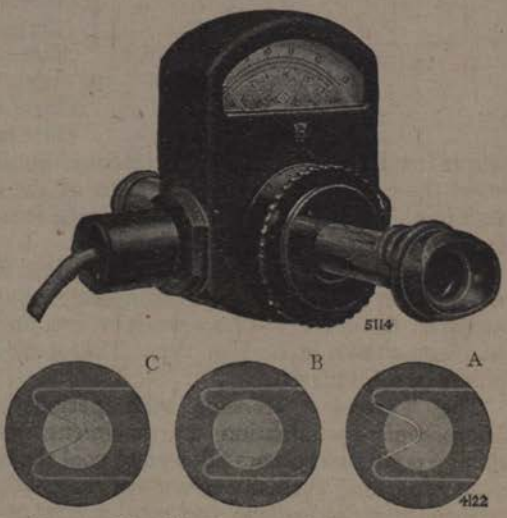
Courtesy of the Integra Co., Ltd.]

FIG. 175.

lished them, the instrument can ensure their maintenance without resorting to tiresome and unnecessary calculations for correction.

Curves may be constructed for permanent reference.

Uses of Pyrometers. — Metallurgical practice has been almost revolutionised since it became possible to determine high temperatures accurately and to obtain continuous records. Coke ovens, gas flues, hot-blast stoves, mains, and flues, waste gas (down comers), furnace operations of all kinds (smelting, annealing, processing), pouring temperatures of cast metals, malleableising, hardening, and tempering operations and many others can all be checked by suitable pyrometers permanently installed with recording appliances or periodically by portable instruments.



Courtesy of Cambridge Instrument Co.]

FIG. 176.—Disappearing filament pyrometer. Showing appearance in use. A, filament too hot; B, correct; C, filament too cold.

The forms described are those principally used. Thermo-couples are easiest to install for fixed installations, various types of recorder being used.

The progress of metallurgical research during recent years has been dependent on pyrometric work. The discovery of "critical" points in solid metals and the changes in properties that accompany them have reduced the manipulation and processing of metals to a scientific basis, and brains not brawn are responsible for results.

Cooling Curves.—If a protected thermal junction be immersed in a bath of molten tin or other pure metal, the temperature noted and the metal allowed to cool down, readings being taken at regular intervals (½ minute or 1 minute), and plotted on squared paper, it will be observed that the dots give an unbroken straight line curve until solidification begins and the temperature ceases to fall.

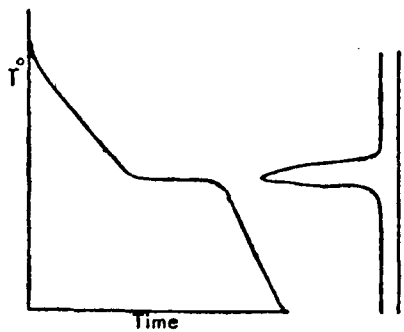


FIG. 177.

During the solidification the temperature remains constant, and the curve plotted from observations is a horizontal line. The curve will have the form of A in Fig. 177. When the metal has become solid the rate of fall in temperature again becomes constant but a little slower than during the first period. This break in the curve is taken as a reference point for calibrating purposes. If tin be used the point indicated on the scale of the instrument is equivalent to 231·5°. Similarly, other points can be found, and the scale divided in accordance with the determination.

If the *rate* of cooling be plotted against time—*i.e.* the number of degrees per interval—instead of actual temperatures, so long as it is uniform, the curve will be a straight line, and we shall get a curve of the form shown in B, Fig. 177. This form is often used for critical points in solid metals.

The "arrests" coincide with periods of changing structure. Microscopic examination on specimens quenched just above the change point, and others allowed to cool though the T° range without quenching, may furnish evidence of the change.

Steel quenched above the recalescence temperature is a case in point. See p. 180.

Temperature Indicators.—The use of substances of known melting-point, such as pure metals and alloys of definite composition, as a means of ascertaining temperatures of furnaces is one of the oldest methods employed. Platner and Princep used pellets of metal resting in cells in a clay support in 1828.

Such adventitious methods are sometimes very serviceable.

A form in which the principle is still employed is the "Seger

Cone." These cones are made of mixtures of silicates and other bodies very carefully adjusted to melt at fixed temperatures, the melting-point of the mixture being accurately determined. They are made up in thin triangular pyramids. The melting-points of the mixtures increase by a rise of some 20° C. Thus No. 28 melts at 1630° C., 29 at 1650° C., 30 at 1670° C. The thicker ends of the pyramids are inserted in a block of refractory material so as to stand upright. This block is inserted in the furnace in a convenient position, the "cones" being sheltered to prevent damage. When the "squatting" temperature is reached they sag and melt. By using a series of cones, say 6 in the same block, the highest temperature reached is indicated. Watkins' temperature recorders are of the same character made up in pellet form.

NOTABLE TEMPERATURES

Sun, lowest estimate	6000° C.
Electric arc furnace	3600°
Oxy-hydrogen flame	2800°
Oxy-acetylene	2400°
Bunsen flame (maximum)	1888°
Platinum melts	1755°
Molybdenum melts	2500°
Tantalum melts	2850°
Tungsten melts	3267°
Iron	1530°
Fluor melts	902°
Coal ignites	400°
Wood	300°

MELTING-POINTS OF REFRACTORIES

Firebrick	1500–1600° C.
Bauxite	1600–1800°
Silica (Quartz)	1750°
Chromite	2000–2150°
Alumina	2050°
Carborundum	2450–2550°
Lime	2570°
Magnesia	2700–2800°
Zirconia	2600–2700°

POULET'S TEMPERATURE SCALE

Incipient red	525° C.
Dull red	700°
Incipient cherry red	800°
Cherry red	900°
Clear cherry red	1000°
Deep orange	1100°
Clear orange	1200°
White	1300°
Bright white	1400°
Dazzling white	1500° upwards.

METALLOGRAPHY

Metallography is concerned with the internal structure and disposition of the components of the material forming the mass of metal, both free elements, solid solutions and compounds. Sometimes the structure is of such a nature as to be readily made visible, by suitable preparation, to the naked eye more or less completely. This is described as the macrostructure (Gr. *makros*=long, great). See Fig. 23.

Generally, and in any case, there is always a minute structure that can only be revealed by microscopic magnification—the microstructure (Gr. *mikros* = small, little).

Micrographic methods include all the necessary means to prepare the material for examination—polishing, etching, heat treating or other treatment.

Permanent records of the results rendered visible in either case may be recorded by photographic means. In the case of deeply etched macrostructure ordinary inking type-printing methods are possible. See Fig. 23.

Since the introduction of metallographic methods of examination it has become abundantly clear that the properties and behaviour of metals are due to the character of the structure, and the changes in structure brought about by changes in heat and mechanical treatment mainly, but also by other forces. Such changes may be permanent or reversible, depending on the metal and the conditions.

Static and Mobile Equilibrium.—In order to appreciate metallographic changes, it is necessary to bear in mind that static conditions only represent the mean positional attitude of material that is always in motion, and size, shape, and properties are dependent on the preservation of a particular attitude. This may be the joint result of a number of causes, chemical and physical, of varying intensity, and changes take place when the conditions become so much altered as to overcome the joint effect. Critical points occur when sudden release takes place.

This idea of internal movement[1] will make clear the possibility of rearrangement taking place in the solid state when conditions favouring an increase or diminution in the amount of movement (latitude), such as heating and cooling, are made to alter. The effects of mechanical or other strain in changing structure and properties by forcibly interfering with the mutual relationships of the molecules forming the mass is also clear.

Structure.—The final structure of a metal or alloy is the ultimate effect of the treatment and conditions through which it has passed.

All metals—except those which are obtained by agglutination and welding methods (see tungsten, p. 330), are produced in or pass through the molten state and, as noted (p. 6), tend to become crystalline on cooling, producing either definite crystal forms or

[1] Roberts-Austen described an experiment in which gold penetrated a lead cylinder resting on it, gradually penetrating to the top of the cylinder, under normal conditions.

crystalline grains depending on the properties of the metal and conditions of cooling. There is no amorphous (non-crystalline) (Gr. *amorphos* = shapeless) metal produced on solidification. The tendency while solidifying is for material of the same kind to attach itself to the solid already formed and to dispose itself as the crystallising forces of the system to which it belongs determine.

Since solidification depends on cooling and loss of heat by the system, it follows that where bodies of higher and lower freezing-points exist in admixture, or can be formed by the mutual reaction of the components, the substance or substances having the higher freezing-point will begin to separate first, leaving the others in the still molten mass forming the mother liquor.

Substances of a foreign character and all that tend to lower melting- and freezing-points will be rejected or thus remain in the liquid to a later stage of the cooling. As pointed out above, solidification and crystallising proceed as heat is lost and most rapidly inwards in the direction opposite to that by which the heat passes out. Hence, where rapid cooling occurs, there is a tendency to produce a columnar structure on the outside of the mass. See Ironfounding, p. 148.

Retarded cooling. — Where cooling is retarded and the metal cools down uniformly—conductivity being sufficiently good to transmit the heat lost and unify the temperature in all parts of the molten mass—a balance being struck between the amount lost and that transmitted—it is possible for the whole main mass of metal to reach the solidifying point and pass slowly through the change to a solid state, conductivity as before maintaining practically uniform temperature throughout the mass, the latent heat (see p. 16) given out assisting in retarding the cooling of the mass.

FIG. 178.—Rejected matter round grains.

This is the condition favouring the beginning of crystallisation at many centres throughout the mass noted on p. 6. Crystallisation proceeds independently from each centre, developing a minute area of crystallisation extending towards other centres, Fig. 164. The area thus affected is more or less spherical, and as crystallisation proceeds, these areas come into contact. The intervening fluid metal is finally appropriated and the whole becomes a mass of polygonal grains, Fig. 5, which represents compressed or restricted spheres the size of which has very important effects on properties—the metallic grains. Sometimes this condition can be actually observed.

This may result from the warming of the mould material reducing the rate of heat loss by lowering the temperature gradient, or by the

establishment of a wall of the solidified hot metal sufficiently thick to protect the interior in the same way. Warming moulds has been exploited as a means of influencing structure in the production of pearlitic cast iron.

During this solidification impurities and rejected bodies are pushed toward the outside of the grain and finally form more or less complete films enveloping the grain or may be more or less completely pushed into the corners forming the angles of the grain and appear as shown in Fig. 178.

This effect is not confined to impurities and insoluble matters, but also applies to bodies of varying solubility so that solid solutions which have a lower freezing temperature remain fluid. The crystallites first forming to produce the grain will contain the minimum amount of the alloying element—may in fact only consist of the metal of higher melting-point. As the temperature falls the crystallites will tend to contain a larger proportion of the alloying element till at the end only material representing the lower limit of solubility may remain fluid.[1] There is no doubt that during the period of solidification interchange of components takes place between the solid phase and that remaining liquid. The former take up more of the alloying metal while the liquid re-absorbs some of the earlier formed solid. This interchange may go forward to completion, the grain being finally quite uniform in character, like Fig. 10.

Very often it is incomplete and traces of the original crystallisation remain visible on examination—"coring" referring to the first part of the crystallisation forming the core of the grain. By heat treatment—in this case maintaining the metal near the melting-point, the core may be in many cases completely obliterated by diffusion.

The above also explains the possibility of two or more solutions of different composition limits, being formed as cooling proceeds, and also the production of eutectics, which are further referred to later and on p. 337.

Critical Points.—It was stated above that metals retain their qualities and character until conditions are set up which destroy the equilibrium or enable a different equilibrium to be established.

Thus, in heating a metal, it remains solid till the fusion point is reached. When that temperature is attained and the heat supply continued, solid equilibrium changes to fluid equilibrium, which will be maintained so long as the heat conditions are maintained above the melting-point. With volatile metals another change occurs at the boiling-point of the metal.

No rise in temperature above the melting-point occurs until the whole of the metal is melted.

These are points easily distinguishable and are the most easily recognised critical points, *i.e.* temperatures at which definite changes in the properties of the metal occur. They are readily observed because of the changes of state which occur and the relatively large

[1] Solid solutions were defined on p. 9.

amounts of heat involved—latent heat. Many other changes take place in metals which do not involve a change of state or of large quantities of heat, but do correspond with very great differences in properties. Like the changes of state in fusion or vaporisation they do occur at definite temperatures and are accompanied with an absorption or evolution of heat dependent on whether the temperature is rising or falling. Most of them are reversible, and on heating take place at a slightly higher temperature than on cooling owing to the slowness with which the necessary molecular rearrangements take place in the solid state.

The amounts of heat are small and can only be detected by pyrometric observation.

These critical points mark physical changes taking place in the metal either in crystalline character or solubility. They are thus intimately connected with the properties and working possibilities of the metal.

Frequently they are associated with striking micrographic changes, and the changes indicated by the pyrometer can be verified by microscopic examination and, conversely, marked changes of structure may point to critical points which must be sought.

Perhaps the most striking example of such changes is evidenced by steel in which both changes in the metal and the solubility of the carbide of iron are concerned.

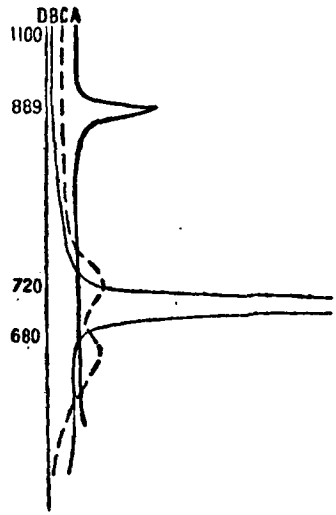


FIG. 179.

Fig. 179 is a pyrodiagram indicating the behaviour of pure iron medium carbon and high carbon steel and manganese steel on cooling from 1100° C. A—pure iron—shows that at 889° C. the cooling stopped for a period—a definite critical point—although heat was being lost at the same rate as before. That lost was being replaced by the heat given out by the physical transformations taking place in the metal. B is a medium (0·4 carbon) steel. It will be seen that no change occurs at 889°, but begins at a lower temperature and is completed about 680°. C is a hard (1·3 carbon) steel. The temperature falls to nearly 680° before a very prolonged arrest begins, and below that temperature cooling proceeds normally. D is a manganese steel. No arrests in the cooling curve occur, no heat-releasing changes taking place.

Note.—It should be borne in mind that all the heat which causes these arrests of cooling is already resident in the metal, but at the temperature above the change point is in the same relative condition as latent heat in a liquid.

When pure iron is heated any changes must be merely physical. The relatively small break at 889° C. is due to a change in the crystalline character—the transformation of γ iron to α iron. In B (mild steel) the introduction of carbide of iron into the system has prevented the iron undergoing change at 889° C., and lowered the temperature at which it begins.

Note.—This is due to the fact that the carbide prevents the change in crystallisation taking place until the internal strain is such that it ultimately overcomes the resistance.

With more carbide the retarding influence is increased and a lower T° 690° is reached before the structure breaks down under the strain.

The manganese present completely prevents the change occurring.

The microscopic examination shows what is taking place in the carburised iron. If a specimen of the steel be quenched in ice cold water from 1100° C. to prevent the structural changes as it cools, it will be found to be a uniform solid solution, austenite, and may be quite as simple in structure as the pure iron, though much harder.

If specimens be allowed to cool slowly and then examined, the low carbon steel will present the appearance in Fig. 13, and the high carbon in Figs. 14 and 97. The difference in appearance is due to the fact that although the carbide of iron is soluble in the γ iron—*i.e.* the "hot" variety, it is insoluble in α iron into which the metal passes on cooling. (With carburised iron, *i.e.* containing only carbon, this limiting temperature γ is 690°, below which γ iron cannot exist) and separates out. Between this temperature and the temperature at which α iron changes to γ iron the amount of carbide retained in solution varies from about 27 per cent. (1·8 C.) to 13·0 per cent. (= 0·89 per cent. C.). When high carbon steel cools after exposure to high temperature—austenitic state—as cooling proceeds the carbide in excess of that capable of retention separates as free cementite, often in borders round the grains, Fig. 14. This rejection continues until the temperature reaches the transformation point—in this case the "recalescence point." When this point is reached the iron still retains 13·0 per cent. of Fe_3C = 0·89 per cent. C. in solution, but when the change occurs this is completely precipitated and separates out in more or less intimate association with the iron, sandwiched in fact in layers when slowly cooled. The banded appearance in E Fig. 97 is due to the edges of the plates being cut across in the section. Heat is evolved in its separation, and the heat which produces recalescence is the sum of that given out by the transformation of the iron and the separation of the carbide.

Diagrams embodying the results of metallographic examinations are constructed. They indicate the critical points, compositions at various temperatures, and the final result. In the case of steel and in the working of other metals they indicate the best treatment to produce the result required.

The behaviour of metals when alloyed together can be similarly

recorded, the influence of alloying metals on the melting-point and the character of the solid matter being indicated—an equilibrium diagram.[1]

If observations are taken of the temperature at which solidification begins in each of a series of alloys of any two metals and the temperature at which solidification is completed, the results can be plotted as shown in the diagram 1, Fig. 180. This illustrates the principal general features of equilibrium diagrams for binary alloys. Above the liquidus all is fluid; between the liquidus and solidus solid and liquid exist in admixture; below the solidus solidification is complete. The formation, composition and range of a eutectic and the final state of the solid alloys of varying compositions, are indicated. The nearness or remoteness of any alloy to the eutectic composition will determine the relative proportions of the components, free metal, solid solution, or eutectic.

Such a diagram for lead and antimony is shown in 2, Fig. 180.

Percentages of the two metals are indicated on the base line, Pb being reckoned from E and Sb from D. The normals represent T °

The temperatures at which mixtures of varying proportions of lead and antimony begin to solidify are used to construct the " liquidus " curve ABC, the mutual effect in lowering the M.P. being indicated by the inclination of the branches of the curve, 100 per cent. lead melts at 327° C., 100 per cent. antimony at 632° C. Addition of one to the other lowers the M.P., and the two branches finally intersect at B (the eutectic). Pyrometric readings of all alloys between D and E, except B, give two indications of arrests in the rate of cooling, the first at a temperature which indicates the beginning of solidification, furnishing the point for the liquidus line, and the second all at the same temperature—the temperature at which the eutectic B solidifies. This last arrest becomes more prolonged as B is approached in either direction and the first less noticeable.

All alloys are solid below the temperature indicated by DE. B is the eutectic composition. It does not begin to solidify till that temperature is reached and remains stationary till solidification is complete.

All alloys of lead and antimony above the liquidus curve are entirely fluid.

Between the liquidus and solidus the metal is partly solid and partly liquid, the proportions varying at any given temperature. At all temperatures above the M.P. of the eutectic, there will be some fluid.

Examination of the diagram will show that the eutectic range at 246° C. extends right across from 100 per cent. antimony nearly to 100 per cent. lead. Its termination at the lead end coincides with a proportion of 2·45 per cent. antimony and 97·55 lead at the solidifying-point of the eutectic. That represents the maximum amount of antimony that can exist in solution at that temperature. The fact that antimony does not retain any lead in solution after solidification

[1] So called because it records the conditions of equilibrium at different temperatures in different proportions.

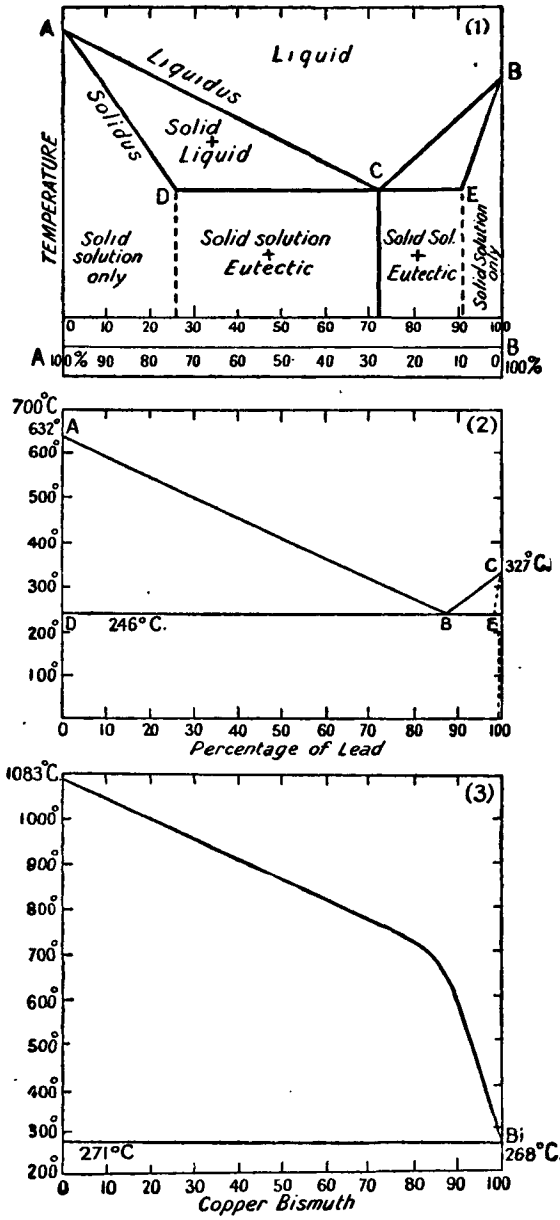


FIG. 180.—Equilibrium diagrams. (1) General equilibrium diagram; (2) antimony-lead alloys; (3) copper-bismuth alloys.

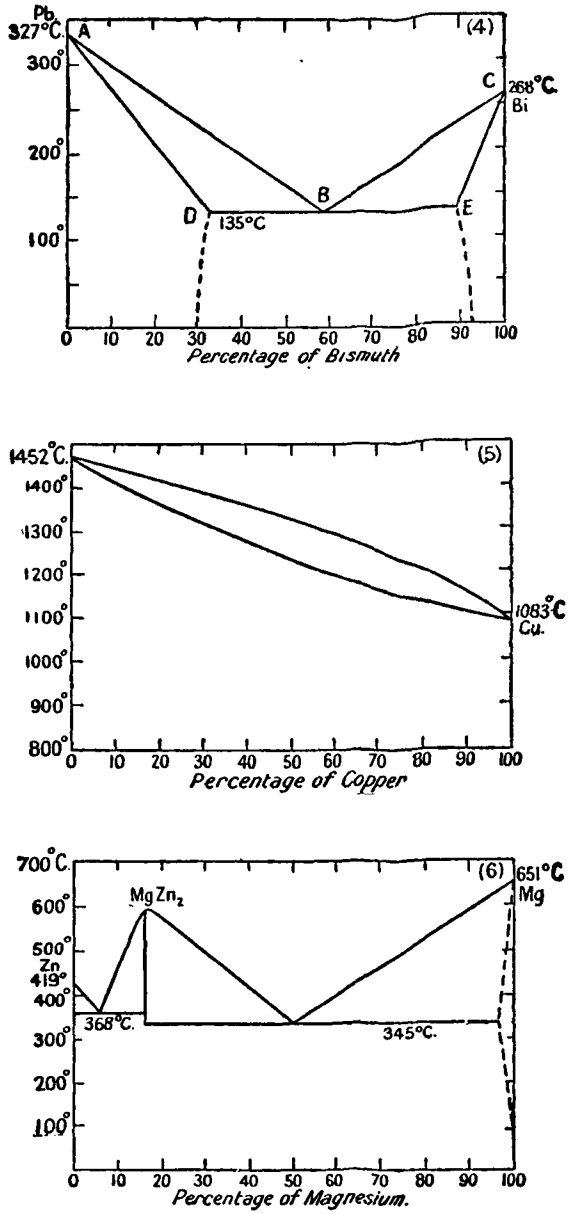


FIG. 181.—Equilibrium diagrams. (4) Lead-bismuth alloys; (5) nickel-copper alloys; (6) zinc-magnesium alloys.

is indicated by the eutectic range extending to 100 per cent. antimony. All solidification taking place in alloys containing more than the eutectic proportion of antimony, about 13 per cent., is due to the separation of pure antimony leaving the fluid alloy richer in lead till the eutectic proportion is reached and solidification is completed. Similarly all solid separating from alloys containing less than 13 per cent. antimony, is a solid solution ranging from pure lead beginning to separate at 327° to a solid solution of 2·45 antimony at the eutectic temperature. The solidified mass on the antimony side of B consists of metallic antimony and eutectic. On the lead side of B it consists of eutectic and a solid solution of lead and antimony.

Reference to the diagram will show a line extending below the eutectic branch, gradually approaching the 100 per cent. limit of lead. This records the fact that after complete solidification has taken place, as the temperature falls the solubility of antimony in lead falls still farther, and at ordinary temperatures is only 0·25 per cent., so that in the very slowly cooled alloy the lead and antimony exist almost completely as separate metals.

The materials in the eutectic being insoluble separate on solidification, producing either granulation or platy structure. When these plates are cut across in preparing specimens for microscopic examination, the characteristic banded structure is observed. All mixtures of two metals do not produce eutectics. If the amount of the alloying metal does not exceed the proportion that can be retained in solid solution, no eutectic will be formed until the proportion exceeds that amount.

Fig. 181 (4) shows the lead-bismuth diagram in which the metals are partly soluble in each other but form a eutectic. ABC is the liquidus as before, and ADEC the solidus. The proportions included between D and E include all mixtures capable of producing the eutectic. Alloys containing a larger proportion of bismuth than D, or of lead than E, produce no eutectic, but form solid solutions at the solidus temperature.

All lead alloys containing a greater proportion of bismuth than D will contain some eutectic. All bismuth alloys containing a greater proportion of lead than E will contain some of the same eutectic.

The composition of the solidified portion varies as previously stated. At any stage of cooling the composition of the solid part is the alloy containing the largest proportion of the more readily fusible constituent that can remain solid at that temperature, and the liquid portion contains the minimum proportion which will ensure fluidity (always an increasing amount as the temperature falls), a balance being maintained as the cooling proceeds.

Equalisation by exchange of constituents between the liquid and solid portions goes on, so that finally if the cooling has been prolonged there is little difference in composition between the portion that solidified first and the last portions to solidify before the eutectic stage is reached.

Fig. 181 (5) is an example of metals completely soluble both in the liquid and solid conditions and forming no eutectic.

Fig. 181 (6) indicates how the formation of a compound may affect the behaviour. Each metal forms a eutectic with the compound.

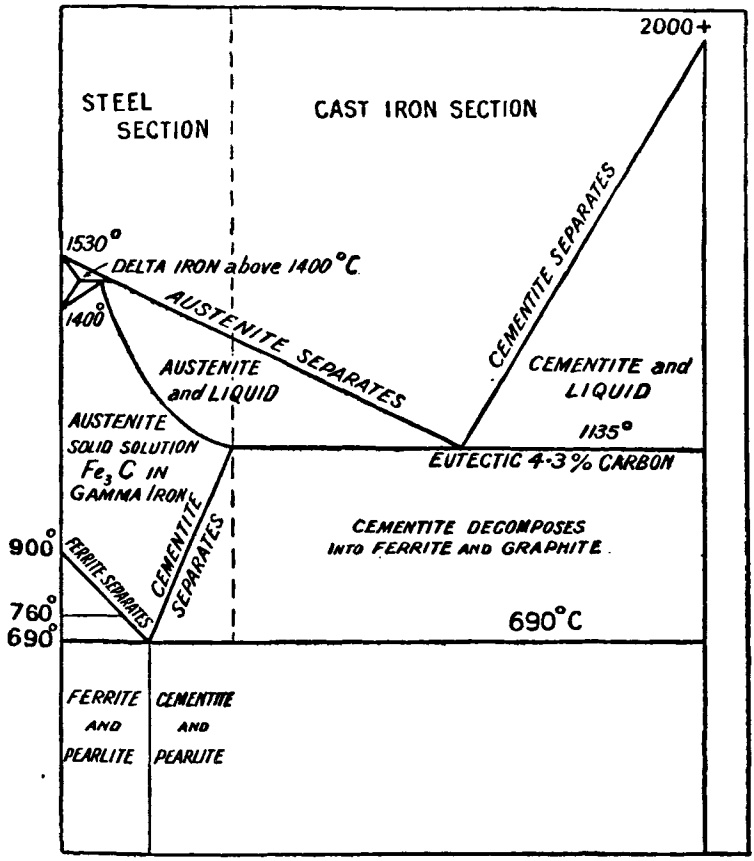


FIG. 182.—Iron-carbon diagram.

Alloys on the zinc side of the diagram contain when solid a eutectic of the compound and zinc, on the magnesium side a eutectic and magnesium. There is slight solubility of the compound in magnesium but not in zinc.

Changes after Solidification.—The solubility of a metal in the solid state may vary with the temperature. All the metal, in perfect solution at the moment of solidification, may not remain in solution as the alloy cools. The completeness of the separation may be affected by slow cooling or prolonged heating below the solidus D'E when

separation similar to that taking place when the eutectic solidifies may take place and be detected by microscopic methods. Often changes in the rate of cooling below the solidus in alloys near the end of the eutectic series indicate that such changes are taking place and may be detected by pyrometric methods. Points indicated by the alloys concerned may be plotted below the line in the manner shown by the dotted lines. They show the change in composition of the solid solution of the metals.

These and all similar diagrams are built up by a collaboration of pyrometric and microscopic examinations.

The arrest points indicated by the pyrometer are plotted and the structure and changes in structure sought and confirmed by the microscope.

Upon the results obtained, mainly by the use of these instruments, the enormous advances in physical metallurgy have been based.

Every observed change in character and every condition to which metals are subject has been or is being made the subject of research and the data systematically recorded.

PRINCIPAL ELEMENTS AND ATOMIC WEIGHTS [1]

Aluminium	Al	27		Molybdenum	Mo	96	
Antimony	Sb	120		Nickel	Ni	58·7	
Arsenic	As	75		Nitrogen	N	14	
Barium	Ba	137·4		Osmium	Os	191	
Bismuth	Bi	208		Oxygen	O	16	
Boron	B	11		Palladium	Pd	106·7	
Bromine	Br	80		Phosphorus	P	31	
Cadmium	Cd	112·4		Platinum	Pt	195	
Calcium	Ca	40		Potassium	K	39	
Carbon	C	12		Rhodium	Rh	103	
Chlorine	Cl	35·5		Rubidium	Rb	85·5	
Chromium	Cr	52		Selenium	Se	79·2	
Cobalt	Co	59		Silicon	Si	28	
Copper	Cu	63·5		Silver	Ag	108	
Fluorine	F	19		Sodium	Na	23	
Gold	Au	197		Strontium	Sr	87·6	
Hydrogen	H	1		Sulphur	S	32	
Iodine	I	127		Tantalum	Ta	181	
Iridium	Ir	193		Tellurium	Te	127·5	
Iron	Fe	56		Tin	Sn	119	
Lead	Pb	207		Titanium	Ti	48	
Lithium	Li	7		Tungsten	W	184	
Magnesium	Mg	24·3		Uranium	U	238·5	
Manganese	Mn	55		Vanadium	V	51	
Mercury	Hg	200		Zinc	Zr	65·4	

[1] These are approximate for purposes of calculation.

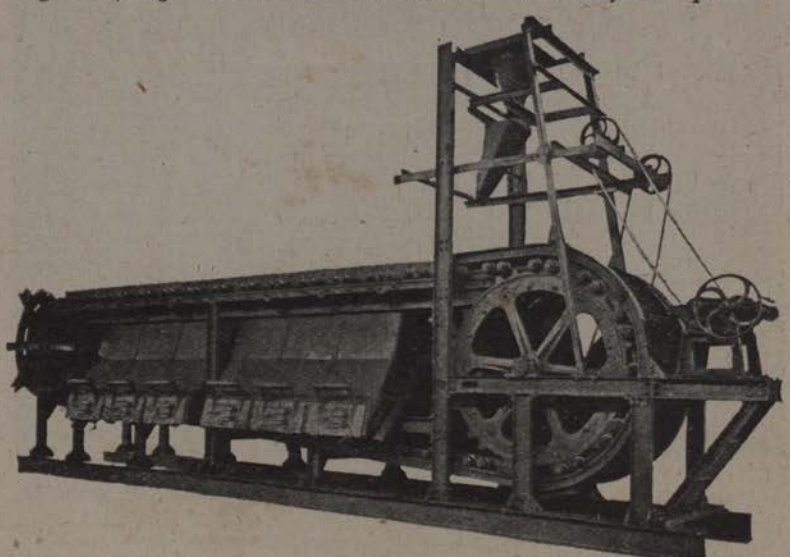
APPENDICES

SINTERING IRON ORES

In blast furnace practice much attention has been given in recent years to methods of preparation which enable finely divided material to be agglomerated so as to fit it for charging into the blast furnace. It is necessary that the sintered material shall be uniform in character and porous, so that rapid smelting may be combined with the production of a uniform grade of iron and steady output. Finely divided concentrates of Scandinavian magnetites, mill scale, pyrites cinders from sulphuric acid manufacture, and various finely divided ores—otherwise rejected or giving trouble in the furnace—and flue dust can be successfully agglomerated.

In general the fines—which may be a mixture of fine ore and other materials—are mixed with coke breeze very carefully and thoroughly, and placed on grates forming the bottoms of shallow trays, ignited, and subjected to an air current. The burning of the coke heats the mass. Partial reduction takes place and a more or less compact porous mass results. The trays are tilted to remove the contents. Any fines are separated and the fritted material sent to the blast furnace.

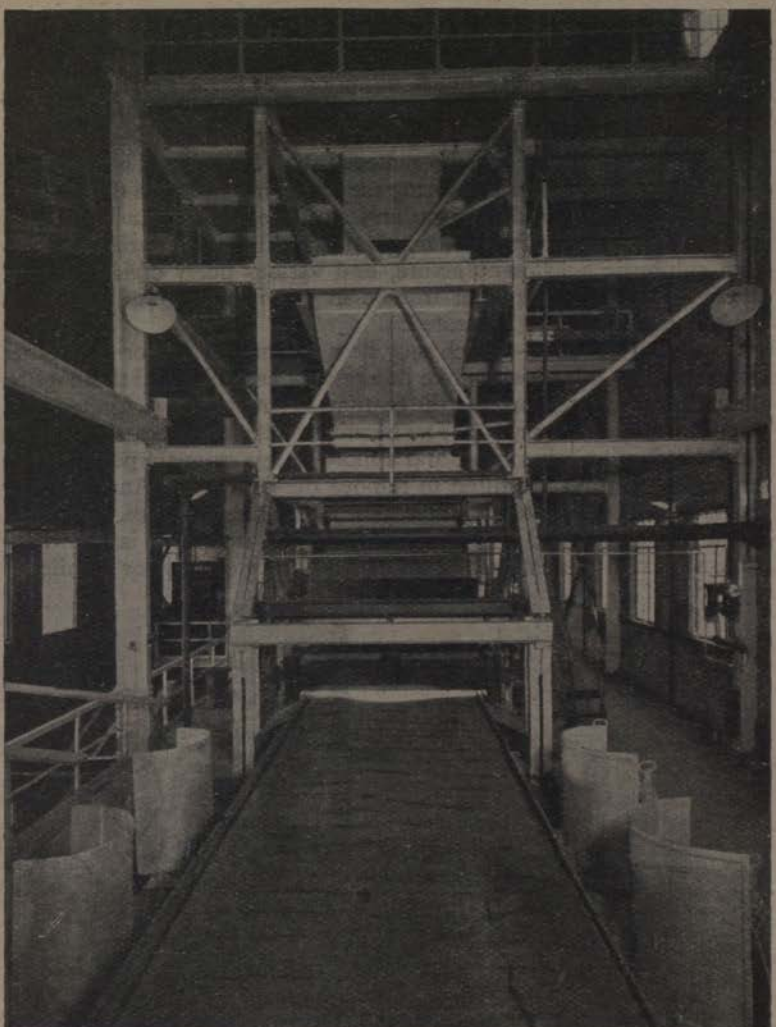
The Dwight Lloyd sintering machine for iron ores is shown in Figs. 182, 183. It consists of an endless chain of trays or "pallets"



[By the courtesy of Iron and Coal Trades Review.

FIG. 182.—Dwight Lloyd Sintering Machine.

mounted as shown on a framework, so as to form a flat table with low walls at the sides. The pallets travel on rollers and are driven by a sprocket roll at the "feed" end of the frame, returning underneath,



[By the courtesy of Messrs. Huntington, Heberlein & Co., Ltd., London.

FIG. 183.—The Dwight Lloyd sintering machine in operation, showing the flat table formed by the pallets, and the methods of ignition and feeding.

upside down. The "sinter" is discharged when the pallets turn over at the end, falling on an inclined screen "grizzly," with bars $\frac{3}{4}$ inch apart.

This removes the material too fine to go forward. It is returned to the mixing plant. Coarse material goes to the furnace.

Under the table formed by the "pallets" is a series of "wind" boxes connected with an exhaust fan which sucks a current of air downward through the mass and passes the products of combustion through dust chambers to the stack.

The material is fed to the pallets from hoppers at the sprocket end. A layer of coarser material, consisting of the coarser particles of fine sinter separated by the grizzly, or of limestone chippings is placed on the bars as a dressing or hearth layer. This protects the iron bars and prevents the charge from sticking. The ore and coke mixture containing a suitable amount of moisture to prevent dusting is delivered from another hopper and levelled. Mixing, moisture content and levelling must be well done to produce good results.

As the charged pallet moves forward over the first wind box it passes under a special ignition chamber heated by blast furnace gas or other means. The surface of the charge is ignited and the hot gases are sucked downwards. The evenly glowing charge moves forward and, as the combustion extends downwards through the material, fritting takes place. If too hot, clinker forms and destroys porosity. If too cold, fritting is poor, and much of the charge will be returned to the plant for retreatment.

The sulphur in pyrite cinders containing 4 per cent. sulphur can be reduced with satisfactory treatment to 0·2 per cent. or less.

The speed of the moving pallets is so adjusted as to ensure proper sintering and the cooling of the material before discharge.

Many machines with capacities up to 1,000 tons of "sinter" per 24 hours are in use.

POWDER METALLURGY

This deals with the production of metallic masses by the compression and working of metals in powder or fine granules as distinct from fusion and electrolytic processes, thus producing exemption from most of the laws and conditions governing fused metals and alloys.

It is possible to produce compact masses with properties similar to those attained by fusion processes. In some cases the metallic particles weld together perfectly with probably subsequent diffusion. Such metals may have tensile strength and ductility comparable with ordinary forms of the metal. For some metals, as in the case of tungsten and tantalium, it is the only way of obtaining ductile metal for wire and sheet.

It is possible also by this method to produce compact masses of intimately associated metallic masses of metals which do not alloy in the liquid state, such as copper and lead, and to produce a uniformly porous material which retains oil and forms good bearing metal by ensuring lubrication, owing to the admixture of hard and soft metals.

It is even possible to incorporate in the mixture of powdered metal non-metallic substances such as graphite and other bodies. Even cast iron has been built up in this way.

In many cases the product is due to the welding together of the particles—or something closely allied. In such cases all the conditions relating to welding must be observed. Oxidation must be prevented, and the material may require heating to a suitable temperature with subsequent working. In this way the workable forms of tungsten, molybdenum and tantalum are obtained, the particles being sintered together; whether welding, in the ordinary sense, occurs or not, particle adhesion takes place producing a structure that is not inferior in strength to that produced by ordinary intercrystalline bonding in ordinary metals.

Some metals, like platinum and gold, weld with the greatest ease. Prior to the introduction of the oxyhydrogen blowpipe for its fusion, compact platinum was obtained by making a paste of platinum black with water, putting the paste into a wrought iron container—like the nut for a bolt—heating in a smith's forge, and hammering as in forging iron. Pure gold welds so readily that, if, in beating, gold leaves are allowed to come into contact, they cannot be separated without tearing the leaf. In these cases oxidation does not occur.

It is essential in most cases that oxidation should be prevented and any heating necessary must be carried out under reducing conditions. Provision is made so that during heating and compression reducing gases shall permeate the porous mass of particles in the container. It is obvious that any film of oxide would prevent that intimate contact necessary for the adhesion of the particles. In making tantalum, the powder compact is heated in vacuo electrically to avoid oxidation or contact with gases. As the particles sinter during heating or when pressed together, shrinkage will occur as the spaces between the particles—voids—are obliterated.

The temperature to which the powdered material is subjected varies with circumstances. The mixture may be heated to the fusion point of one or more of its components, thus allowing for dispersion or localised fusion between adjacent particles and produce alloy parts or articles practically in their final form. Powder metallurgy lends itself to (1) the formation of aggregates; (2) the production of unusual structures; and (3) uniformity, owing to the absence of liquation.

The hard carbides of tungsten, molybdenum and tantalum can be included in a suitably tough binder alloy without impairing the hardness of the carbide. Similarly welding electrodes of high conductivity copper and electrodes containing tungsten are produced by suitably balanced powders.

Powder products of silver with graphite, and with nickel, tungsten or molybdenum, furnish contacts for electrical "make and break" purposes. The admixture of metals, which it would be difficult to

alloy, and the retention of their properties in the aggregates produced are important considerations in powder metallurgy. Such aggregates do not possess the ordinary structure of cast alloys. Cohesion is secured by adhesion or welding of the particles. This limits the grain development of the structure, grain growth, such as may occur in liquefied and cast metals being impossible. The final structure depends on the size of the initial particles of the metals employed. The extent to which diffusion occurs will be dependent on temperature, pressures and time. Ordinarily the diffusion may be small and limited to the surface of the particle.

Bimetallic electric contacts are an example of special structures. Powdered copper is placed in a suitable mould, a layer of silver and graphite added and the whole pressed and sintered to a compact form.

The copper-tin-graphite bearings to replace gun-metal bearings are made in the same way. The metal mixture is formed in a mould and pressed cold, thus yielding a uniformly porous mass. The mixture is heated and when hot quenched in oil. In quenching the oil enters the pores from which air has been expelled and saturates the mass. The continuity of the pores makes the bearing oil retaining.

Structure of the " powder " products is under control to a much greater extent than fused alloys in castings. Fusion and dispersion only occurs at the surfaces of adjacent particles, and the unsatisfactory structure and properties of the " as cast " structure are avoided, a fine grain being maintained throughout. This probably accounts for many of the exceptional results obtained in some cases. In most cases of exceptional strength, where the metals in the powders are not easily weldable, some fusible constituent is present, and during heating and pressure fills the voids, producing solidarity.

The production of alloys, or substitutes for alloys, having the same composition is possible. Electrical conductivity of products is high. Hard silver-nickel contact alloys having a conductivity 75 per cent. that of silver have been prepared.

The production of powders sufficiently fine for this purpose is not easy. Mechanical reduction by stamp, ball mills, etc., has many objections. Aluminium, cadmium, zinc and brass have been disintegrated by stirring during the brittle stage when solidifying.

Fine granules are also produced by atomisation. Steam or compressed air, previously superheated to the melting point of the metal, is directed through a nozzle partly submerged at the surface of the molten metal. The stream of particles produced is carried off under suction to collecting devices. There is little oxidation even with aluminium and zinc, less than 0·2 per cent. of oxygen being present. The method can be used up to 700° C.

In other cases a stream of molten metal falling from an orifice is met by a pressure jet of steam or air at right-angles to its fall. The resulting powder is collected as before.

Metal powders are also produced by the reduction of the oxides electrolytically and in other ways.

VALORISATION

Fuming Processes.—In the last few years much attention has been paid to processes in which the metals to be recovered are first separated as fume, either as oxides or sulphides, leaving a residue of clinker or waste.

These methods are applied to raw ores and concentrates and to slags and leached residues from electrolytic treatment. Complex residues containing zinc, lead and tin on the one hand and on the other such metals as copper, silver, gold, nickel and cobalt may be thus treated.

A shaft furnace, for which preheated air is used, attains a temperature of nearly 1,800° C. The furnace has a charging chamber at the top and large gas outlets. Hot air at 500° C. is supplied through water-cooled tuyères.

The gases containing the volatilised compounds pass through dust catchers and (*a*) Cottrell fume collectors to recover zinc, lead and tin oxides, or (*b*) through wet scrubbers of the tower and screen type, finally through a Theisen centrifugal scrubber. "Wet" precipitated material is settled and the slimes filtered on an Oliver filter and sent forward for treatment.

The residual gases are used to preheat the air blast and for other purposes. If wet methods of recovery have been used they are previously dried.

At Baelen slags—of long standing—containing :

Zn . . .	8·6 per cent. lead
Pb . . .	2·5 „ „ „
Cu . . .	0·4 „ „ „
SiO_2 . .	34·0 „ „ „
FeO . .	30·0 „ „ „
CaO . .	11·5 „ „ „
Ag . . .	3·5 (approx.) grm. per ton.

yield fume, matte and slag as follows :

	Fume.	Matte.	Slag.	
Zn	51·5	1·2	1·5	per cent.
Pb	16·0	2·9	0·6	„ „
Cu	0·5	5·5	0·15	„ „
Fe	—	58·0	23·0	„ „
Ag (grams/ton)	5 to 270.0	—	—	
SiO_2 . . .	5·0	—	33·0	„ „
C	3·5	—	—	„ „
S	3·0	24·0	2·5	„ „
Sn	0·03	—	—	„ „
Sb	0·01	—	—	„ „
CaO . . .	—	—	15·0	„ „

After calcination the fume is passed on for electrolytic treatment. The matte is treated for copper.

At St. Denis a plant is being built to treat residues containing 2 per cent. tin. In tests 90 per cent. of the tin has been recovered.

Waelz Process.—In the Waelz—literally "trundling motion"—process volatilisation of the metals is carried out in a long rotary kiln which revolves slowly—about 2 revolutions per minute. The kilns vary from 40 ft. long 6 ft. diameter to 160 ft. long 12 ft. diameter, turning on bearings, with a slope varying from 2–4 per cent. of the length. The cylinder is lined with fire brick or magnesite brick.

The material is mixed with coke or other fuel and fed at the higher end of the kiln. It need not be finely ground. The coke breeze usually varies from 20 to 25 per cent. Calamine or other oxidised ore may be treated in the raw state, but sulphides need a preliminary roasting. Charges of roasted ore containing Zn 37·5, Cu 7·5, Pb 1·03, Fe 24·1, S 5·5 per cent. contain 25 per cent. coke. Charges of lead furnace slag containing Zn 20, Pb 1·5, Cu 1·5, S 7, FeO ·36 per cent. contain 28 per cent.

With calamine the proportion is 23 per cent. coke. The kiln is "self-burning," air entering at the lower end, which is open. In starting up the kiln oil or gas heating is provided, but in operation, unless some hitch occurs in the descending material, the combustion and reactions occurring in the mass provide all necessary heat. In the lower part of the cylinder the air entering cools the material and carries heat inwards; at the higher end, the freshly charged material is partially heated by the escaping hot gases.

Moisture in the charge absorbs some of the heat.

The reaction zone is in the middle part of the kiln.

The reactions taking place may be typified as follows:

$$ZnO + C = CO + Zn$$
$$Zn + O = ZnO$$
$$CO + O = CO_2$$
$$C + O_2 = CO_2$$

Quantities of heat absorbed and evolved in the two former reactions balance each other so that fuel is only required to maintain the temperature of the kiln.

The temperature of the kiln rises to 1,100°–1,200° C. The emerging gases leave at 500°–600° C.

The gas flow through the kiln, from 35 to 50 cu. ft. per second, is controlled by a fan operating beyond the fume collecting plant. The gases are passed into dust chambers and after cooling to 200° C. proceed to the baghouse or to Cottrell electrical precipitators.

The charge becomes heated to the volatilisation point of zinc, 930° C., as it travels forward—approximately one-fifth of the kiln's length.

The reduction, volatilisation, and burning of the liberated zinc take place over the whole surface of the tumbling charge and continues over some 80 per cent. of its length. The greater part of the kiln has a dazzling incandescence due to the burning of the escaping zinc and the gases produced by the reaction, the two phases of reduction and oxidation taking place in the same part of the kiln. The fume produced by the burning metal can be seen ascending to the outlet end of the kiln.

The fume varies in composition according to the character of the ore:

From	Zn.	Pb.	Tin	Copper
Lead slags . . .	66·5	6·5	—	—
Zinc muffle slags . .	58·8	9·2	—	—
Roasted blende . .	60·8	14·5	—	—
Brass ashes . . .	63·9	11·6	—	—
Zinc+copper ore . .	75·3	—	0·7	0·21

The presence of tin and the practical absence of copper in the fume may be noted

Note.—In recent years much attention has been paid to the volatilisation of tin and recovery of fume.

In the new plant at the famous Mansfeld works in Germany Waelz kilns have been installed to deal with the slags from the copper smelting furnace. The argentiferous copper ore carries less than 1 per cent. zinc and less than 0·5 per cent. lead. These are volatilised and oxidised in the smelting together with some sulphide. The fume is collected. It contains up to 27 per cent. lead, 26 per cent. zinc, 0·8 per cent. copper and 0·2 per cent. silver.

By mixing this with 10–15 per cent. of raw lime and passing the mixture through a Waelz kiln carefully heated by powdered lignite, no fuel being added, the lead in the charge is volatilised *as sulphide*, which burning in the current of hot gas is oxidised, the oxide being recovered by electrical precipitation as usual. This fume may contain 49 per cent. lead and 9 per cent. Zn. The clinker passing from the Waelz may contain less than 3 per cent. lead and 35 per cent. zinc. Sulphur is present in both fume and clinker. The clinker contains about 20 per cent. lime. The lead fume together with dust from the lead smelter is sintered and smelted for lead and silver.

The zinc clinker mixed with the lead slags containing zinc (20 per cent. Zn) is passed through a second larger Waelz kiln to recover the zinc as oxide fume, from which the zinc is recovered. The kilns have a capacity of 55 tons of slag in 24 hours. The lead slags at Mansfeld were allowed to accumulate. These are gradually being worked up.[1]

Volatilisation from Molten Slag.—At Traill, in Canada, molten slag from the lead furnace is "fumed" in a water-jacketed furnace. The slag is introduced in a molten state. Dust coal is employed as fuel. It is supplied by dual tuyères and enters the furnace side by side with the air supply, *i.e.* one side of the tuyère supplies coal dust and the other side air. They bubble up together through the molten slag. Lead and zinc in the slag are reduced at the outer surfaces of the bubbles where their oxides and the coal dust come into contact. The volatilised metals rise and escape to the top of the charge and burn in the excess of air. The hot gases are carried forward through cooling flues with dust pockets to Stirling boilers which utilise the waste heat and generate power for blowing and vacuum purposes. The gas and uncondensed fume pass through Green's economisers for further cooling on to the

[1] W. H. Harris, A.I.M.E., Vol. 121.

baghouse, where the uncondensed fume is recovered. Similar reactions to those occurring in the Waelz kilns take place.

The furnace is 24 ft. long, 10 ft. high, 10 ft. wide with 35 dual tuyères on each side. Molten slag is introduced from pots by a launder at one end 6 ft. from the bottom of the furnace. Treated slag is tapped from the end of the furnace opposite the charging launder.

The charge is from 60–65 tons and its treatment takes approximately 2½ hours and recovers 85 per cent. of the zinc and 98 per cent. of the lead present. Treating 600 metric tons per day each 1 per cent. recovered represents 6 tons of the metal. The slag treated contains 3·6 per cent. lead, 16·3 per cent. zinc. The fume recovered varies from 9 per cent. lead to 16·6 per cent., while the zinc varies from 25–67·7 per cent. Silver recovery is about 62 per cent. of that present in the slag.

Fume is recovered and removed at all possible points on the way to the baghouse.

The baghouse consists of six 10-compartment units of 18 flannel bags each, and the gases enter at approximately 250° F. and about a pressure of 2 inches of water.

The fume is treated electrolytically for the recovery of the metal.

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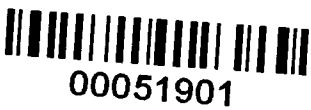
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